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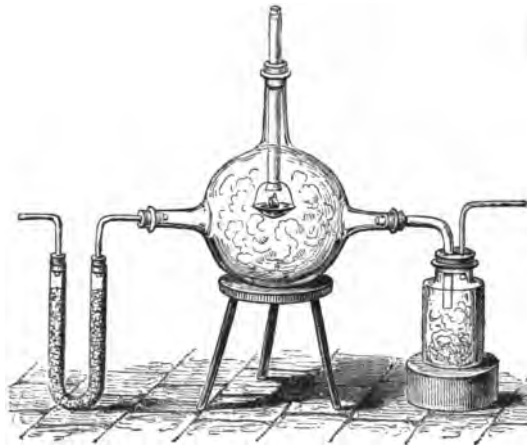
CHEMISTRY FOR SCHOOLS

BY Dr. LARDNER.



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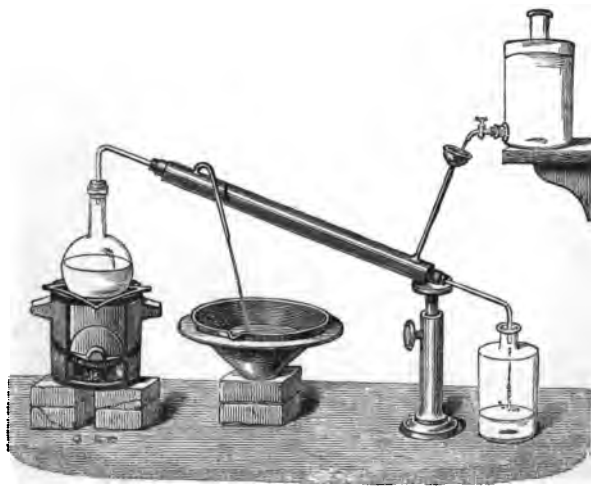

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CHEMISTRY

FOR

SCHOOLS.

BY

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PREFACE.

THIS compendium is one of a series of books of elementary instruction for the use of Schools and families, of which two have already been published, one on Natural Philosophy, and the other on Animal Physiology, and it is compressed within similar limits of bulk and price. It comprehends so much of the elements of chemistry as may, with moderate attention, be acquired within a reasonable time by the younger class of students, and even as much as may suffice for those who, being more advanced in life, desire merely to obtain a general knowledge of the elements of the material world, and of the chief compounds into which they enter.

The importance of a perfect familiarity with the system of notation now adopted by chemists of all countries, and which, therefore, constitutes an universal language, cannot be too strongly impressed on beginners. By this notation their progress will not only be immensely expedited and facilitated, but the pleasure they will receive in prosecuting their study of the science will be greatly augmented. Indeed, it may be truly said that, in the actual state of Chemistry, no serious progress can be hoped for without the aid of this admirable notation,

which, moreover, is so extremely simple, that it may be perfectly mastered by a few hours' attentive study. The Teacher should, therefore, exercise his pupils in it carefully for some days before he allows them to proceed further in their studies.

The study of the "Natural Philosophy for Schools" should precede that of the present compendium, inasmuch as several of the subjects contained in it, such, for example, as Heat and Electricity, are necessary to enable the Student to comprehend many of the processes of Chemistry.

As in the Author's other Works for Schools, the Table of Contents prefixed to this volume is so composed that the Teacher may form from it Questions for the examination of his class, the Answers to which will be found in the corresponding paragraphs of the volume.

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CHEMISTRY FOR SCHOOLS.

CHAPTER I.

PRELIMINARIES.

1. BODIES are *simple* or *compound.*

2. A SIMPLE body cannot, and a COMPOUND body can be resolved by known means into two or more bodies differing from each other and from the whole.

3. Ex.: Gold, silver, lead, charcoal, and sulphur cannot be so resolved, and are therefore simple. Water, salt, and lime can be resolved, the first into two gases, and the last two into a gas and a metal, and they are therefore compound.

Bodies classed as simple at one epoch in the progress of science, prove to be compound at a later epoch, means of resolving them being discovered. The term *simple* must therefore be taken, not in an absolute, but in a relative sense.

4. ANALYSIS * or decomposition is the process by which a compound is resolved into its components.

5. SYNTHESIS * or composition is the contrary process by which two or more different bodies are brought into combination, so as to form a compound different from themselves.

6. Simple bodies are called *elements.*

7. THE ELEMENTS, which are the materials of which the world is composed, are 62 in number, of which 49 are classed as metals, the other 13 being called metalloids.†

8. The names of the elements and the letters or symbols by which for brevity they are expressed are as follow. The import and use of the numbers annexed to them will be explained hereafter.

* From ἀνάλυσις (analysis), and σύνθεσις (synthesis), Greek words of the same meaning.

† According to the French chemists generally, the metalloids are 15 and the metals 47, arsenic and tellurium being regarded by them as non-metallic. The term metalloid, a Greek derivative signifying "like a metal," has been objected to. It is, however, generally adopted both by British and foreign chemists.

METALLOIDS—13.

* Oxygen .....O	8	* Carbon C	6	* Fluorine .....F	18·9
* Hydrogen .....H	1	* Chlorine Cl	35·5	* Boron .....B	10·9
* Nitrogen, or azote N	14	* Bromine .....Br	80	* Silicon .....Si	21·3
* Sulphur .....S	16	* Iodine I	127·1	Selenium .....Se	39·5
* Phosphorus .....P	32				

METALS—49.

* Potassium (Kalium) .....K	39·2	* Manganese ....Ma	27·6	Iridium .....Ir	99
* Sodium (Natrium).....Na	23	* Iron (Ferrum) ..Fe	28	* Platinum .....Pt	98·7
* Lithium L	6·5	* Cobalt .....Co	30	* Gold (Aurum)..Au	197
* Barium .....Ba	68·5	* Nickel .....Ni	29	Osmium .....Os	99·6
* Strontium .....Sr	43·8	* Zinc .....Zn	32·6	Titanium .....Ti	25
* Calcium .....Ca	20	* Cadmium .....Cd	56	Columbium(Tantalum).....Ta	92
* Magnesium ....Mg	12·2	* Lead (Plumbum) .....Pb	103·7	Pelopium .....Pe	?
* Aluminum.....Al	13·7	* Tin(Stannum) ..Sn	59	Niobium.....Nb	?
* Glucinum .....G	26·5	* Bismuth.....Bi	71	Norium .....No	?
Yttrium.....Y	32·2?	* Copper (Cuprum)Cu	31·7	Tellurium .....Te	64·2
Zirconium.....Z	22·4	* Uranium .....U	60	Tungsten (Wolfram) .....W	95
Thorium.....Th	59·6	* Mercury(Hydrargyrum) .....Hg	100	Molybdenum ..Mo	46
Cerium C	47	* Silver (Argentum) .....Ag	108	Vanadium V	68·6
Lanthanium ....La	47?	Palladium .....Pd	53·3	* Chromium.....Cr	26·7
Dydimium.....D	49·6	Rhodium .....R	52·2	* Antimony (Stibium).....Sb	120·3
Erbium .....E	?	Ruthenium ....Ru	52·2	* Arsenic .....As	75
Terbium.....Tb	?				

These elements, whether considered as materials out of which the Earth is formed, or with relation to their application to the uses of life, vary much in importance. Those which are not marked with an asterisk, are without importance in either respect; and of those which are so marked, not more than 14 or 15 enter to any considerable extent into the composition of the Earth. The others, such as gold, silver, platinum, and so on, though they derive importance from their uses in the arts, are so rare, and exist in such comparatively minute quantities, that they may be altogether disregarded as component parts of the Earth.

We shall, therefore, in the present volume limit our notice chiefly to those elements which are marked in the table with an asterisk.

9. ATOMS are the smallest particles into which a body can be conceived to be resolved without decomposition.

Although all bodies, whether simple or compound, are capable of division without practical limit, each part however minute into which they are divided being identical in character, properties, and composition with the whole, certain chemical phenomena and the forms assumed in crystallisation show that all bodies do consist of certain ultimate molecules which admit of no further subdivision, and which therefore have received the name of atoms.*

10. A compound body consists of compound atoms, the components of which are the atoms of the components of the compound.

EX.: The atoms of water are formed by the combination of the atoms of the two gases which by their combination form water.

* "Ατομος (atomos), a Greek word signifying "an indivisible thing."

11. MIXTURE. When two bodies being in the liquid or gaseous state are mixed together so that their atoms become mutually interfused without exercising any chemical action on each other, the mass is called a *mixture*. In this case the atoms remain as independent of each other as when the two bodies were completely separated. They are merely in juxtaposition without combination.

The volume of a mixture is therefore equal to the sum of the volumes of the bodies mixed.

The properties of a mixture partake of the properties of the bodies mixed, those of neither body being effaced.

Ex.: The atmosphere is a mixture of two gases. Any volume of it is equal to the sum of the volumes of the two gases which it contains, and the properties of the one gas are not effaced, but only diluted and rendered less intense by the presence of the other, as spirits are diluted and weakened by mixture with water.

12. COMPOUNDS. When two bodies combine one with another, atom with atom, the volume of the compound is seldom equal to the sum of the volumes of the components, and the properties of the components are generally effaced altogether from the compound.

Ex.: If the two gases of which the atmosphere is composed be mixed together in the proportion of 200 cubic inches of the one (nitrogen) to 500 of the other (oxygen), the mixture will resemble atmospheric air, consisting of the same gases though mixed in a different proportion. Its volume will be 700 cubic inches and it may be respired without injury. But if the gases thus mixed be made to enter into combination (which may be effected by suitable methods), the gaseous mixture will be at once converted, if water be present, into the liquid called in chemistry *nitric acid*, and in commerce *aqua fortis*, thus completely losing the properties of the mixed gases and acquiring a new and totally different character.

13. COHESION is the force by which the atoms of a body are held together, upon the intensity of which the mechanical qualities of hardness, toughness, and so on, depend.

14. AFFINITY is the force by which the atoms of components are united together to form the atoms of a compound.

Affinity exists, not only between the atoms of different simple bodies, in virtue of which they unite to form compounds, but also between the compound atoms of different compound bodies, so as to make them enter into combinations and form compounds of still more complex composition.

Ex.: The atoms of the metal *potassium* have an affinity for those of the gas *oxygen*, in virtue of which they combine to form *potash;* and the atoms of *nitrogen* have an affinity for those of *oxygen*, in virtue of which they combine to form *nitric acid*. In like manner the compound atoms of *potash* and those of *nitric acid* have a mutual affinity, in virtue of which they combine to form the more complex compound called in chemistry *nitrate of potash*, and in the arts *nitre* or *saltpetre*.

CHAPTER II.

LAWS OF COMBINATION.—NOTATION.

15. Bodies capable of being mixed together may be mixed in all proportions.

Ex.: The atmosphere is a mixture of the gases oxygen and nitrogen in the proportion of 20·8 parts by weight of oxygen to 79·2 of nitrogen. But an infinite variety of other mixtures of the same gases may be produced by interfusing them in other proportions. In fact, they may be mixed together in any proportions whatsoever.

16. Bodies combine chemically only in certain definite numerical proportions.

Ex.: The same gases, a particular mixture of which forms the atmosphere, are incapable of entering into combination in the proportion in which they are thus mixed, nor in any of the infinite variety of other proportions in which they may be mixed, with the five following exceptions:—

1° 14 parts by weight of nitrogen combine with 8 of oxygen to form a gas called *nitrous oxide*, more commonly known as *laughing gas*.

2° 14 parts of nitrogen combine with 16 of oxygen to form a gas called *nitric oxide*, wholly different in character and properties from the former.

3° 14 parts of nitrogen combine with 24 parts of oxygen to form a very volatile liquid called *hyponitrous acid*.

4° 14 parts of nitrogen combine with 32 of oxygen to form a yellowish liquid called *nitrous acid*.

5° 14 parts of nitrogen combine with 40 of oxygen to form the liquid called in chemistry *nitric acid*, and commonly known as *aqua fortis*.

Now it will be observed, that the proportions in which oxygen enters into this series of compounds are expressed by an arithmetical progression of multiples of 8. If N be taken to express 14 parts by weight of nitrogen referred to any proposed ponderable unit, and O express 8 of the *same units* of oxygen, the series of compounds above may be thus expressed:—

Nitrous oxide	N + O
Nitric oxide	N + 2 O
Hyponitrous acid	N + 3 O
Nitrous oxide	N + 4 O
Nitric acid.	N + 5 O

It may be shown that no combination can be formed by nitrogen and oxygen in any proportion intermediate between any two of these, or in any proportion above or below those of the extreme limits of the series. If any agency having the power of exciting combination, be applied to a mixture in which the two gases are found in any proportion other than one of the five above indicated, combination will take place according to one or other of the proportions exactly expressed in the above series, and the surplus of the gas not necessary to make up the definite numerical proportion will retain its gaseous state uncombined.

17. The law thus manifested among the compounds of nitrogen and oxygen is one of very general though not absolutely invariable prevalence in chemical combination. It may be thus stated:

If a body A combine with another B in more than one proportion, its combinations will form an arithmetical series of multiples of one of its components; so that if A and B express the lowest combining ratio, the other combinations will be found in the series $A+2B$, $A+3B$, $A+4B$, and so on.

It sometimes happens however that combinations take place in other numerical proportions, which do not form a regular arithmetical series, but which nevertheless are still explicable on the principle of multiples. Thus 2A may combine with 3B forming the compound 2A+3B or 3A with 4B forming the compound 3A+4B or 2A with 5B, forming 2A+5B and so on. These complex proportions are however comparatively rare.

18. CHEMICAL EQUIVALENTS. Bodies not only form combinations in this regular progression of multiples, but form compounds the components of which can be expressed in weight by constant numbers, so that the combining proportion of the same body with all others shall be expressed by one and the same number.

To illustrate this, let any proposed weight of hydrogen gas be taken as the the unit or standard of combining proportion. The least weight of oxygen with which this will combine will be expressed by 8, that is, it will be 8 times the weight of the hydrogen which is the unit. This combination will form water.

If a combination of the same unit of hydrogen be made with sulphur, it will be found to combine with 16 parts of that body, forming a gaseous compound called sulphuretted hydrogen.

Relatively to hydrogen as the unit the combining weight of sulphur would therefore be 16.

If the compounds of sulphur and oxygen be examined, it will be found that they consist of 16 parts or multiples of 16 parts of sulphur combined with 8 parts or multiples of 8 parts of oxygen, all such numbers having still for their unit the standard weight of hydrogen.

The same being found to be true for other combinations, it follows that, taking hydrogen as the unit, 8 will be the combining weight of oxygen and 16 of sulphur.

By a like process it may be shown that 14 is the combining weight of nitrogen, 6 of carbon, 32 of phosphorus, and generally that the combining proportions of all elements are the numbers severally annexed to them in the table, § 8.

CHEMICAL EQUIVALENTS is the name given to these numbers. The equivalents of compounds are found by adding together those of their components.

Ex.: Water being a compound of one equivalent of hydrogen (1) with one of oxygen (8), its equivalent is $1+8=9$.

Ex.: Vitriol being a compound of one equivalent of sulphur (16) and three of oxygen, its equivalent is $16+3\times8=40$.

19. ATOMIC THEORY. The remarkable manner in which bodies, whether simple or compound, thus combine with each other according to fixed and definite numerical proportions, the same body

always combining with others in the same proportion, has supplied the basis of an hypothesis called the *Atomic theory*, according to which all bodies are supposed to consist of ultimate atoms which cannot be divided at all if the bodies be simple, and only by decomposition if they be compound. The weights of these ultimate atoms when those of any one body are compared with those of any other, are in the proportion of their equivalents. The atoms of compounds are formed by the combination of the atoms of their components, and their equivalents are therefore the sums of those of their components.

In accordance with this view of the constitution of bodies which is now universally accepted, the equivalents are also called *atomic weights*.

The numbers expressing the equivalents or atomic weights of bodies are therefore altogether comparative, expressing, not the absolute weights of the atoms, which are quite unknown, but merely the *proportion* of their weights compared one with another; just as the numbers expressing the specific gravities of bodies express not the absolute but the relative weights of equal volumes of these bodies.

20. The standard or unit of atomic weight therefore, like that of Specific Gravity, is altogether arbitrary. If the weight of an atom of hydrogen be taken as the unit, the atomic weight of oxygen will be 8 and that of sulphur 16. If the atom of oxygen be the unit, the atom of hydrogen will be $\frac{1}{8}$ and the atom of sulphur 2. If the atom of sulphur be the unit, that of hydrogen will be $\frac{1}{16}$ and that of oxygen $\frac{1}{2}$.

Hydrogen has been conventionally adopted by English chemists as the standard unit of atomic weight, and the equivalents of the elements invariably used by them are accordingly the numbers annexed to them in the table, § 8. In foreign works the hundredth part of the weight of the atom of oxygen has been very generally taken as the unit, so that the atomic weight of oxygen is with them 100, that of hydrogen 12·5, that of sulphur 200, and so on. The equivalent or atomic weight of each body according to this convention, may be found by multiplying the equivalent in the table, § 8, by 12·5.

21. LAW OF GASEOUS VOLUMES. When bodies are naturally in the gaseous or vaporous state, or capable of being reduced to that state, a remarkable relation has been shown to exist between the volumes which correspond to their equivalent weights. These volumes are in general either equal or in the proportion of 1 to 2 or 1 to 4.

Thus, for example, if phosphorus or arsenic reduced to vapour be compared under the same pressure and at the same temperature with oxygen, it will be found that the weights of equal volumes will be in the same proportion exactly as their respective chemical equivalents.

If hydrogen, nitrogen or chlorine, be similarly compared with oxygen, it will be found that the weight of a given volume of oxygen will be to the weights of twice the volume of these gases in the exact ratio of their chemical equivalents.

There are certain gaseous compounds, ammonia and nitric oxide for example, the volume of which corresponding to the equivalent weight is four times that of oxygen.

These are the prevailing proportions of the volumes of equivalent weights of gaseous bodies. Other proportions are extremely rare.

This relation between the volumes of equivalent weights of gases is of considerable practical importance, since gases are much more easily measured than weighed, and in many cases the process of measuring may replace that of weighing in experimental researches.

22. NOTATION. The letters annexed to the elements in the table, § 8, are adopted by all chemists, English and foreign, to express the equivalents.

Compounds are expressed by combinations of the letters which express their components not united by the sign of addition +, but written as are the letters of a word.

Ex.: Water, being a compound of single equivalents of hydrogen and oxygen, is expressed by HO.*

When several equivalents of the same element enter into a compound, they are expressed by a corresponding number below the letters.

Ex.: Sulphuric acid (vitriol), being a compound of one equivalent of sulphur and three of oxygen, is expressed SO_3.

Ex.: Nitric acid (aqua fortis), being a compound of one equivalent of nitrogen and five of oxygen, is NO_5.

Ex.: Sesquioxide of iron (rust), being a compound of two equivalents of iron and three of oxygen, is Fe_2O_3.

When a number is prefixed to a compound, it is understood to affect the whole compound, and not merely the component in juxtaposition with it.

Ex.: $10SO_3$ signifies 10 equivalents of the compound SO_3, and not a compound of 10 equivalents of S and 3 of O, which would be expressed thus $S_{10}O_3$.

While compounds are expressed by letters written as those of the same word, mixtures are often expressed by + interposed between the quantities.

Ex.: Thus while HO expresses water, H+O expresses a mixture of hydrogen and oxygen in the proportion in which they form water.

Combinations of two or more compounds are expressed by their several equivalents separated by commas.

Ex.: Saltpetre is a compound of potash and nitric acid. But potash itself is a compound of one equivalent of potassium K and one of oxygen O, while nitric acid also is a compound of one equivalent of nitrogen N and five of oxygen. Potash is therefore KO and nitric acid NO_5. Saltpetre is then KO, NO_5.

* In algebra and arithmetic HO signifies H × O. In chemistry it signifies H + O.

Ex.: Carbonate of soda is composed of 1 equivalent of soda NaO, 1 of carbonic acid CO_2 and 10 of water, and is therefore NaO, CO_2, 10HO.

It is usual in expressing compounds to put the letters which express elements the least analogous to oxygen first.

Ex.: Soda is NaO and not ONa, and salt is NaCl and not ClNa.

CHAPTER III.

NOMENCLATURE.

23. The names of compounds are so formed as to express their composition, and thus to assist the memory.

In the names of the elements certain analogies have been maintained, in accordance with the characters and properties of the bodies named.

The termination *gen* is a Greek derivative signifying the power of making or producing something. The sense of the terms oxygen, hydrogen, and nitrogen, literally given, would be the producers of acid, water, and nitre, of which severally these elements are constituents.

The termination *ine*, common to *chlorine*, *iodine*, *bromine*, and *fluorine*, designed to imply a certain analogy which prevails among the properties of these elements.

The termination *on*, common to *carbon*, *boron*, and *silicon*, indicates a like analogy of properties.

Sulphur, phosphorus, and arsenic are terms of ancient use still retained.

The termination *um*, is, with one or two exceptions, common to the numerous class of metals, the Latin names for several of which are the origin of the symbol expressive of the element. Silicon is by many chemists classed as a metal, in which case it is named *silicium*.

24. Compounds vary much in their degree of complexity. Those of most frequent occurrence in inorganic chemistry consisting of 2, 3, or 4 constituents, are called *binary*, *ternary*, and *quaternary*. Of those, binary are the most numerous and important.

The principal binary compounds are those formed by the combinations of the metalloids severally, and more especially of oxygen with the metals.

The termination *ide* is common to the names of the compounds of oxygen, chlorine, iodine, bromine, and fluorine, severally with the metals, these compounds being called *oxides*,* *chlorides*, *iodides*, *bromides*, and *fluorides* of the metals.

The termination *uret* is common to the compounds of sulphur, carbon, boron, silicon, selenium, and phosphorus, with the other elements and with each other, the names thus formed being *sulphuret*, *carburet*, *boruret*, and so on. Some chemists have recently substituted for these, sulphide, carbide, boride, and so on.

25. When the same elements form several binary compounds, the number of equivalents of one or other constituent is indicated by Greek or Latin prefixes, such as *proto*, *deuto*, *trito*, or *bi*, *ter*, *quadro*, and so on.

In general, the numerical order only of the equivalents is signified by the Greek, while their actual number is indicated by the Latin prefixes. Thus the

* This term was formerly spelled oxyde or oxyd, but the present spelling has been adopted from its analogy to chloride and the names of the other compounds.

binoxide of a metal is one that includes two, the teroxide three, and the quadroxide four equivalents of oxygen. The protoxide includes one equivalent of oxygen, the deutoxide is the next proportion of oxygen in the increasing order, and the suboxide, a compound, if such there be, containing a less proportion of oxygen than one equivalent.

The Latin prefix *per* signifies that the compound includes the greatest number of equivalents of the element with which it is capable of combining.

These rules of nomenclature, so far as relates to the prefixes, are not uniformly adhered to by chemists.

Ex.: The protoxide of silver is AgO, the binoxide AgO_2 which is also the peroxide. The suboxide is Ag_2O.

Ex.: The protoxide of iron is FeO, the sesquioxide, which is also called the peroxide is Fe_2O_3, although there is a higher oxide FeO_3 called Ferric acid.

26. Oxidation in general has a tendency to confer acid properties upon a compound, so that when an element combines with oxygen in several proportions, those combinations which contain the largest proportions of oxygen lose the name of *oxides* and receive that of *acids*.

27. Acids, like oxides, may contain several proportions of oxygen. When there are only two proportions, the higher has a termination in *ic*, and the lower in *ous*.

Ex.: The compound AsO_3 is arsenious acid, and AsO_5 is arsenic acid.

When the same element forms more than two acids by combination with oxygen, the intermediate, lower, and higher acids are distinguished by the prefixes hypo, sub, or per.

Ex.: NO_3 is hyponitrous acid, NO_4 nitrous acid, and NO_5 nitric acid.

Ex.: ClO is hypochlorous, ClO_3 chlorous, ClO_4 hypochloric, ClO_5 chloric, and ClO_7 perchloric acid.

Ex.: SO is hyposulphurous, SO_2 sulphurous, S_2O_5 hyposulphuric, and SO_3 sulphuric acid.

28. Compounds of hydrogen with other elements when they have acid properties are called *hydracids*. Those of sulphur are called sulphacids.

29. Oxides which have acid properties, are sometimes distinguished as oxacids, but more generally called simply acids. Acid compounds of hydrogen or sulphur are always expressed with their proper prefixes.

30. POSITIVE AND NEGATIVE BODIES. When a compound is submitted to the poles of a voltaic pile of sufficient power, it will be decomposed, one constituent being attracted to the positive, and the other to the negative pole. But since electrical attractions are only excited between bodies oppositely electrified, it follows that, at the moment of decomposition, the constituent attracted by the positive pole is in a state of negative electricity, and that which is attracted by the negative pole is in a state of positive electricity.

Since in such decompositions the same element is always attracted by the same pole, it is said to be naturally positive or negative, according as it is attracted by the negative or positive pole.

So long as the compound remains undecomposed, the constituents, being, according to this theory, in opposite electrical states, attract and neutralise each other; but when they are separated, each carries with it its proper electricity, and is attracted by that pole of the pile which is endowed with the opposite electricity.

31. Of all the elements oxygen is the most conspicuously negative, and hydrogen the most conspicuously positive.

In general, when a body, whether simple or compound, is said to be positive or negative, it is meant that, when a compound of which it forms a constituent is

decomposed by the voltaic pile, it will be attracted by the pole of the contrary name.*

32. ACID in its popular sense implies sourness; a quality found in many, though not all, of the class comprehended under the name in chemistry. The production of a red stain upon blue tissues is also a familiar effect of acids, and this is the test of acidity conventionally adopted by chemists.

Paper dyed blue with a vegetable pigment called *litmus* if dipped in any acid liquid will be immediately reddened. If the liquid be not acid, no change of colour will be produced. Such paper is called *test paper*, and is used in the laboratory as the most convenient means of ascertaining the quality of acidity.

33. BASES are a class of compounds having properties opposite to those of acids. Litmus paper reddened by acids will be restored to its proper blue colour if dipped in a basic liquid.

34. NEUTRALS are compounds which manifest neither basic nor acid properties, and which consequently do not change the colour of test paper.

35. SALTS are binary compounds produced by the mutual action of an acid and a base. They are *acid*, *neutral*, or *basic*, according as the effect of their constituents predominate or are balanced.

36. SUBSALTS is a name sometimes given to a basic salt. The names of salts are formed so as to indicate both their constituents. The name terminates in *ate* or *ite* according as that of the acid constituent terminates in *ic* or *ous*, and the name of the base is always expressed after the derivative of the acid.

Ex.: Sulphate of soda is a salt whose acid is sulphuric and whose base is soda. Sulphite of potash consists of sulphurous acid and potash. Hypochlorite of lime consists of hypochlorous acid and lime.

37. The names of acid and basic salts are often so formed as to indicate the proportion of the constituents by their prefixes.

Thus, if the neutral salt be supposed to contain a proportion of acid expressed by 1, the salts which contain proportions of acid expressed by $1\frac{1}{2}$, 2, 3, 4, &c. are qualified by the corresponding prefixes *sesqui*, *bi*, *ter*, *quadro*, &c.

Ex.: The sulphate of potash contains 1 equivalent of the acid; the sesquisulphate, 3 of the acid with 2 of the base; the bisulphate, 2 of the acid with 1 of the base; the tersulphate of alumina, 3 of the acid with 1 of the base.

38. Corresponding names are applied to basic- or sub-salts which are denominated *monobasic*, *sesquibasic*, *bibasic*, *tribasic*, &c. according as they include 1, $1\frac{1}{2}$, 2, 3, &c. equivalents of the base for 1 of the acid.

Ex.: The monobasic nitrate of the oxide of lead contains 1, and the bibasic 2 equivalents of the base with 1 of the acid.

39. When hydracids act upon bases, both constituents are decomposed as will hereafter be explained, and binary compounds are produced, the composition of which has no analogy to that of salts properly so called. These compounds however, having long received the name *salts*, are still so called, but are distinguished as *haloid*† *salts*. Common culinary salt is one of these.

Ex.: When hydrochloric acid HCl acts on soda, NaO, the hydrogen of the former combining with the oxygen of the latter forms water, and the sodium, Na, combining with the chlorine, Cl, is separated as chloride of sodium, NaCl, or common salt.

40. SULPHO- or SULPHUR-SALTS is the name given to combinations of two different sulphurets, one of which plays the part of an acid and the other of a base, the former being called a *sulphacid* and the latter a *sulpho-base*.

* For more full explanation see Handbook of Nat. Phil. "Electricity," and also Nat. Phil. for Schools.

† From two Greek words, ἅλς (hals), *salt*, and εἶδος (eidos), *form*, implying a resemblance to salt, properly so called.

Ex.: The sulphuret of carbon and the persulphuret of arsenic are sulphacids, and are accordingly sometimes called sulpho-carbonic and sulph-arsenic acids. The sulphuret of potassium on the other hand is a sulpho-base, and it forms with these acids sulpho-salts called the *sulpho-carbonate* and *sulph-arseniate of potash*.

41. Salts, properly so called, formed by the combination of an oxacid with an oxy-base are sometimes called for distinction *oxy-salts*.*

In like manner, binary compounds of two different chlorides, iodides, or bromides, are sometimes formed which have the characters of salts, one playing the part of an acid and the other that of a base.

Ex.: The chloride of gold combined with the chloride of potassium forms a double chloride, having the character of a salt, and is called the *chloro-aurate of potash*, or more properly, the *chloro-aurate of potassium*.

CHAPTER IV.

CRYSTALLISATION.

42. With some rare exceptions, all bodies whether simple or compound, in passing from the fluid to the solid state manifest the peculiarity of structure which is expressed by the term *crystalline*; and vast numbers are found, especially in the mineral kingdom, naturally in this condition. When a body in this state is broken, its surface of fracture will present the appearance of a multitude of pointed asperities, which will at first seem to be irregular, but when submitted to the microscope will be found to have a certain uniform geometrical structure.

From this and other observations it has been inferred, that crystallised bodies consist of aggregations of solid particles of regular geometrical figures, all the particles or molecules of the same mass having the same form.

43. When a crystallised body is split, it is found that its division is much more easily effected in some directions than in others. Such directions are called *planes of cleavage*, and are, in fact, parallel to the faces of the component crystals.

The relative direction of the planes of cleavage supply one of the means of determining the forms of the crystals.

* A total change of the manner of viewing the constitution of acids and salts has lately been proposed, and is favoured by many of the highest chemical authorities. According to this system, all acids would be regarded as hydracids, and all salts as haloid salts, analogous to common salt. Hydrogen would be regarded as the true and sole acidifying principle. The adoption of this system would cause a complete change in the nomenclature and formulæ of acids and salts, and would involve the admission of a great number of hypothetical bodies called compound salt-radicals. Whatever be the merits of this system, and they are incontestably very great, it has not yet been adopted in any elementary works, either British or foreign; and its adoption in a volume so very elementary as the present, would be altogether incompatible with the purposes to which the work is more especially directed.

44. The exposition of the properties of crystals forms the part of physical science called *crystallography*, and the processes by which bodies are reduced to the crystallised state are called *crystallisation*.

45. CRYSTALLISATION may be produced artificially by four methods.

1°. BY FUSION. If a body be fused and then permitted to cool by slow degrees until it be solidified it will crystallise.

Ex.: If sulphur be melted and left to cool, a solid crust will be formed upon it. If this be broken and the sulphur which is still liquid be poured off, a beautiful wall of crystals will be seen attached to the sides of the vessel.

46. 2°. BY VOLATILISATION. Certain solids when their temperature is raised to a point below their point of fusion are volatilised. Their vapour thus produced being condensed forms crystals.

Ex.: If arsenic be raised to 356° in a stoneware retort connected with a condenser, it will be volatilised without fusion, and its vapour will be condensed in the form of crystals.

47. 3°. BY SOLUTION IN THE HUMID WAY. A solid being dissolved in a liquid and the solution evaporated, crystals will be deposited when the proportion of the solvent becomes insufficient to hold all the solid in solution.

Ex.: If a solution of sugar be slowly evaporated without agitation, fine crystals of sugar-candy will be deposited.

48. 4°. BY SOLUTION IN THE DRY WAY. This process consists in the use of solvents which have high points of fusion, and which being slowly evaporated in the incandescent state deposit crystals of the body they hold in solution. Ebelman, to whom this method is due, obtained crystals of certain minerals never found crystallised in their native state.

Ex.: Fused boracic acid dissolves most of the metallic oxides. If a mixture of alumina and magnesia in the proportion in which they are found in the mineral called *spinelle* be dissolved in boracic acid fused in a porcelain oven, artificial spinelle will be produced in a crystallised state by evaporating the boracic acid.

49. CRYSTALLINE SYSTEMS. Although they are infinitely various, crystalline forms have been reduced to a very limited number of classes. Some forms are mere modifications of others of a more simple nature. Others are produced by the combination of the more simple forms.

50. CENTRE. Within every crystal there is a certain point which divides into equal parts every line passing through it and terminated in the faces or edges of the crystal. This point is called the *centre* of the crystal, from its analogy to the centre of a circle, which divides the diameters into equal parts.

51. DIAMETERS. Lines passing through the centre and terminated in the crystal are called *diameters*.

52. AXES. Diameters so placed that a plane passing through them will divide the crystal into equal and similar solids, are called *axes*. The crystal is therefore disposed symmetrically around each of its axes.

These axes are distinguished by very important optical properties, which often serve as a convenient method of determining their direction.

All the varieties of crystalline forms have been reduced to six classes called *crystalline systems*, which are severally characterised by the number, relative position, and relative length of the axes.

53. 1°. THE REGULAR SYSTEM has three equal axes, each of which is at right angles to the plane of the other two.

This system includes the *cube* or *regular hexahedron*, *fig.* 1, which has several systems of axes. Thus lines joining the centres of the square faces, and lines joining the opposite angles, are axes.

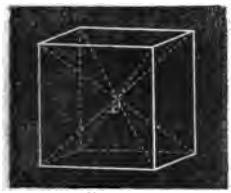


Fig. 1.

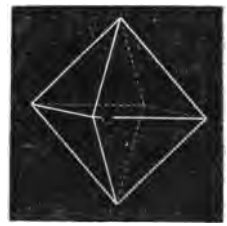


Fig. 2.

It also includes the *regular octohedron*, *fig.* 2, the axes of which are lines joining the opposite angles. Also the *regular rhombic dodecahedron*, *fig.* 3, the *regular tetrahedron* whose faces are four equilateral triangles, *fig.* 4, and various other forms derived from these by modification or combination.

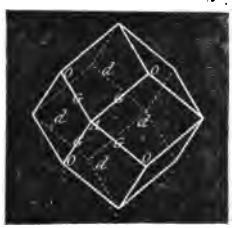


Fig. 3.

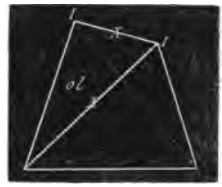


Fig. 4.

54. 2°. THE SQUARE PRISMATIC SYSTEM takes its name from the square right prism, the height of which is greater or less than the edge of its base. In this system there are three axes, each of which is at right angles to the plane of the other two. Two are equal, but the third is greater or less than these.

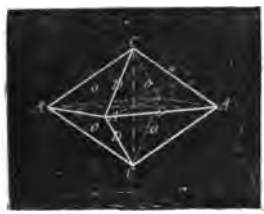


Fig. 5.

Fig. 6.

This system includes, besides the *rectangular square prism*, the *octohedron* with a square base, *fig.* 5, the axes being the two diagonals of the base and the line *c c*.

55. 3°. THE RHOMBOHEDRAL SYSTEM has four axes, of which three are equal, in a common plane, and intersect at angles of 60°, the fourth being at right angles to this plane.

This system takes its name from the *rhombohedron*, *fig.* 6, which is one of its

principal forms. The principal axis *cc'* joins two opposite angles, while the other three or secondary axes join the middle points of the opposite edges.

This system also includes the *regular dodecahedron*, *fig.* 7, the faces of which are 12 equal isosceles triangles standing on a common hexagonal base, the three

Fig. 7.

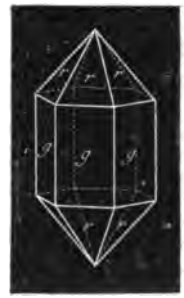


Fig. 8.

Fig. 9.

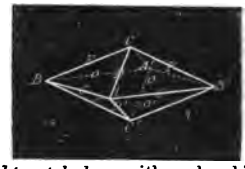
diagonals of which are the secondary axes. It also includes the *right hexagonal prism*, *fig.* 8, and the *dodecahedron*, *fig.* 9, with scalene triangular faces.

56. 4°. THE RIGHT PRISMATIC SYSTEM has three unequal axes, each of which is at right angles to the plane of the other two.

This system takes its name from the *right prism* with a rectangular base, which is one of its forms. The principal axis is the axis of the prism and the lines joining the centres of the opposite lateral faces.

Fig. 10.

Fig. 11.



Another form of this system is the *right octohedron* with a rhombic base, *fig.* 10, consisting of two right triangular pyramids having a common rhombic base. The axis of the pyramids is the principal, and the diagonals of the base the secondary axes.

57. 5°. THE OBLIQUE PRISMATIC SYSTEM has three unequal axes, two of which are oblique to each other, the third being perpendicular to their plane.

This system takes its name from the *oblique rectangular prism*, whose base is a rectangle with unequal sides, its axis being inclined to the base. The axis of the prism is the principal, and the lines joining the centres of its opposite lateral faces the secondary axes.

The octohedron, *fig.* 11, consisting of two scalene triangular pyramids with a rectangle as a common base, belongs to this system.

58. 6°. THE DOUBLY OBLIQUE PRISMATIC SYSTEM has three unequal axes, each of which is inclined to the plane of the other two.

This system includes the *oblique prism* with an oblique parallelogram as a base: the octohedron consists of two scalene triangular pyramids with an oblique parallelogram as their common base.

59. The following are examples of the crystalline forms of the several systems.

1. *Regular system.* Most of the metals, diamond, salt, alum, garnet, fluor-spar, galena.
2. *Square prismatic.* Zircon, tinstone, apophyllite, ferrocyanide of potassium.
3. *Rhombohedral.* Ice, calcareous spar, nitrate of soda, rock crystal, arsenic, antimony.
4. *Right prismatic.* Sulphur (at low temperature), nitre, iodine, sulphates of potash and baryta.
5. *Oblique prismatic.* Sulphur (by fusion), realgar, sulphate, carbonate, and phosphate of soda, borax, green vitriol.
6. *Doubly oblique prismatic.* Sulphate of copper, nitrate of bismuth, quadroxalate of potash.

When the same body is capable of crystallising in different systems, under different conditions, it is said to be *dimorphous*. Sulphur is an example of this.

When two different bodies crystallise according to the same system they are said to be *isomorphous*.

CHAPTER V.

THE LABORATORY.

60. CHEMISTRY, being, more than any other, an experimental science, and the demonstration of all its leading principles depending in the most immediate and direct manner on experiment, it is, above all, necessary that the student in commencing it, be rendered familiar with the implements and apparatus by which experiments are performed, and should also have some general notions of the chief processes resorted to in the development of these principles. For these reasons, we shall here briefly describe the apparatus most commonly used in the laboratory.

Since all chemical action is molecular, it will be promoted by reducing solids to a state of comminution or fluidity. Trituration, solution in liquids, and fusion are therefore frequent operations in the laboratory. The precipitations of solids from their solutions, and their solidification when liquefied, supply means of promoting the peculiar reaction of their molecules. The evaporation of liquids, the volatilisation or sublimation of solids, the condensation of vapours, the evolution of gases from solids or liquids in decomposition by means of chemical or physical agencies, are severally processes of frequent use, and requiring suitable apparatus. The collection, transfer, and measurement of gases also involve peculiar processes and apparatus.

61. TRITURATION, by which the mechanical comminution of solid bodies is effected, is performed by means of mortars, and sometimes by mullets and slabs, *fig.* 12. Mortars differ in magnitude, form, and material, according to the purpose for which they are used. The most common, *fig.* 13, are of stoneware

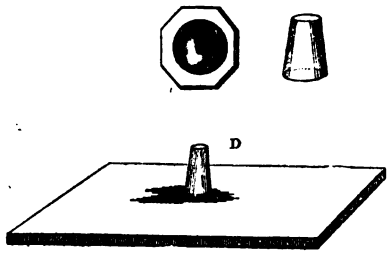


Fig. 12.

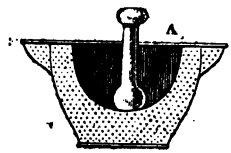


Fig. 13.

or bronze. Small agate mortars, *fig* 14, are used for certain analyses. Steel mortars of peculiar form, *fig.* 15, are used for pulverising certain solids.

A hammer used for fracture and pulverisation is shown in *fig.* 14 A.

Fig. 14.

Fig. 14 A.

Fig. 15.

62. DISSOLUTION. A much more effectual method of separating the molecules of a solid is by dissolving it in a liquid. The liquid in which it can be thus dissolved is called a *solvent*, and when it contains the solid dissolved in it, it is called a *solution* of the solid.

Fig. 16.

Fig. 17.

Fig. 18.

Fig. 19.

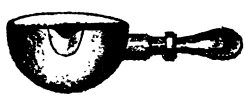


Fig. 20.

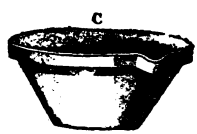


Fig. 21.

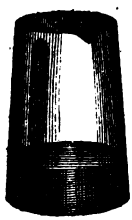
Thus water is a solvent for salt and sugar, alcohol for camphor, and so on. Solids being in general more or less soluble in liquids, according as the temperature of the solvent is more or less elevated, the vessels containing solutions are generally adapted for the application of heat.

Flasks, *fig.* 16, and mattrases, *fig.* 17, of glass of various forms and capacities, capsules of glass, stoneware, or metal, *figs.* 18, 19, 20, pans, *figs.* 21, 22, for

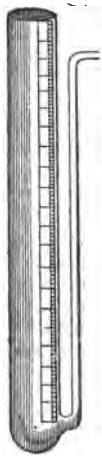
evaporation, glasses for testing, *fig.* 23, and for measuring liquids, *fig.* 24, of cylindrical shape with engraved scales upon them, are provided.

Glass vessels of different forms, tubulated flasks, and graduated tubes, are shown in *figs.* 15 A, 15 B, 15 C, and 15 D.

15 A.



15 D.



15 B.

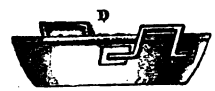


Fig. 22.

15 C.

Fig. 23. Fig. 24.

63. FILTRATION. A process by which a solid body in comminution, held in suspension without dissolution in a liquid, is separated from it by straining the liquid through some body sufficiently porous to allow the liquid, but not sufficiently so to allow the solid particles to pass through it.

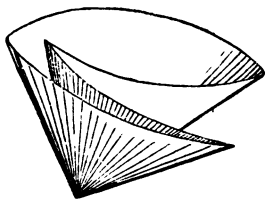


Fig. 25.

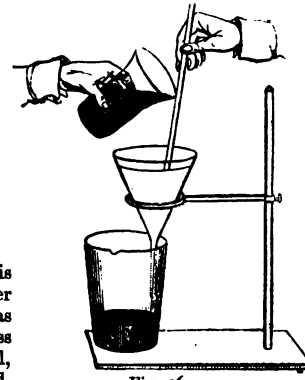


Fig. 26.

Unsized paper called *filtering paper* is much used in the laboratory. The paper being cut in a circular form is folded as shown in *fig.* 25, and then let into a glass funnel conveniently supported over a vessel, *fig.* 26. Before pouring in the turbid liquid, the paper should be moistened with distilled water to swell its fibres, which causes the liquid to pass through clear from the first. The liquid should be directed into the filter by a glass rod.

Other convenient methods of mounting filters are shown in *figs.* 27, 28.

When a precipitate has been deposited from a solution, it is often necessary to wash off the liquid which adheres to its particles. This may be effected by a linen or woollen cloth filter mounted as shown in *fig.* 29.

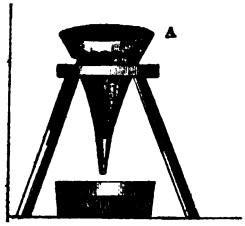


Fig. 27.

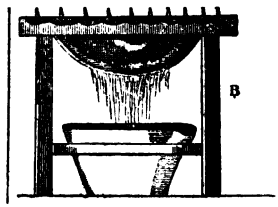


Fig. 29.

64. CHEMICAL STANDS. The necessity of having supports in convenient forms for the objects of experiment will be apparent from what has been already explained, and will be still more so as the student proceeds. Stands and supports of very various forms are accordingly provided in all well-furnished laboratories. They consist generally of brass pillars, on which rings and other supports slide, so as to be capable of adjustment at any desired heights at which

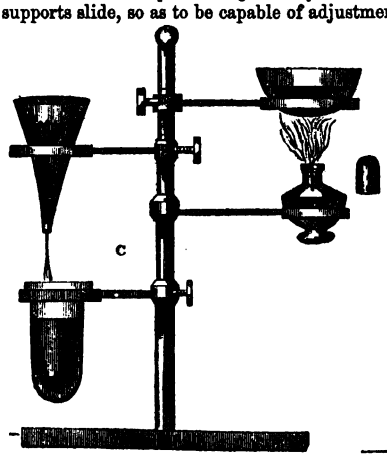


Fig. 28.

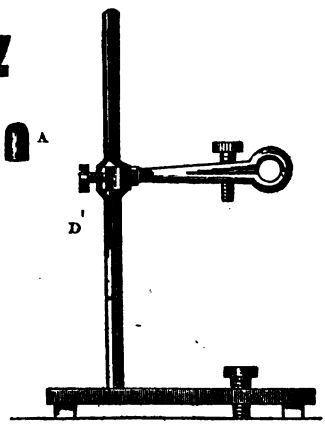


Fig. 30.

they may be fixed by clamping screws. Such a stand is shown in *fig.* 28, furnished with two sliding rings supporting the filtering apparatus C, a capsule with a solution, and a spirit lamp for heating the latter. The glass cap of the spirit lamp to cover it when not lighted is shown at A.

Stands and supports of other forms are shown in *figs.* 30, 31, 32.

65. EVAPORATION AND CONDENSATION constitute the process more commonly known as *distillation.* Its purpose in the laboratory is to separate the more volatile constituent of a compound from the less so. If the two constituents vaporise at

different temperatures, and the compound be raised above that at which the more volatile vaporises, but not so high as that at

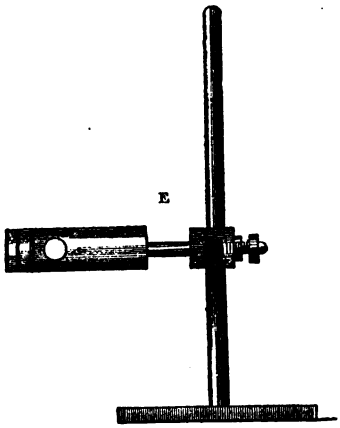


Fig. 31.

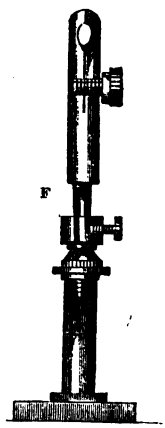


Fig. 32.

which the less volatile vaporises, the more volatile will escape in vapour, the less volatile remaining. The vapour then produced is

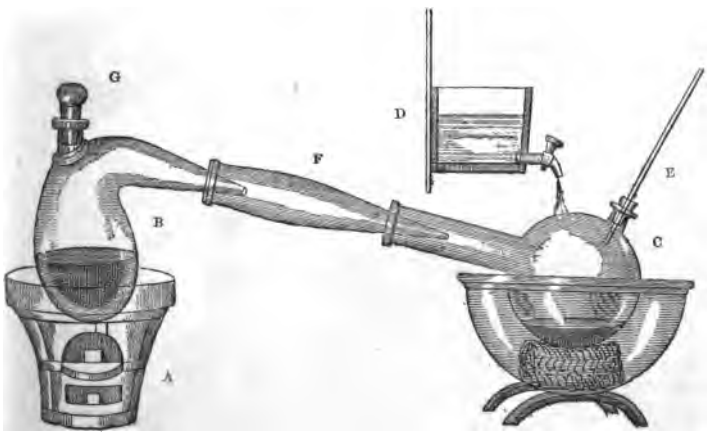


Fig. 33.

conducted by a connecting pipe to a cold vessel in which it is *condensed*, that is, restored to the liquid state by cold.

The apparatus by which this process is conducted varies extremely in form and magnitude, according to the quantity and quality of the liquid to be distilled. One of the most ordinary arrangements is shown in *fig.* 33, consisting

of a furnace A, retort B, connector F, and condenser C, with a vessel D, from which cold water falls on the condenser. A tube, E, is provided for the escape

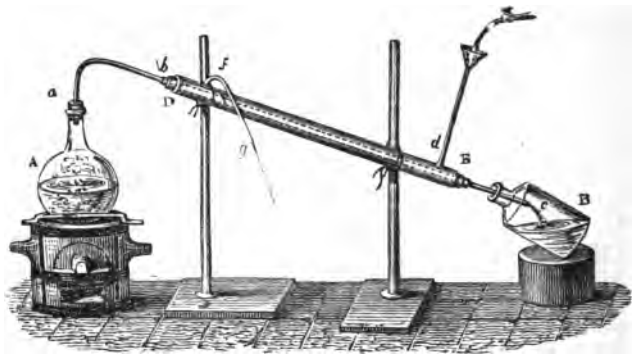


Fig. 34.

of uncondensed vapour and air. A tube with a stopper is placed at G for introducing the liquid to be distilled. A variety of apparatus used in the laboratories at Paris is shown in *figs.* 34, 35. The vapour from *a*, passes to the flask *c*,

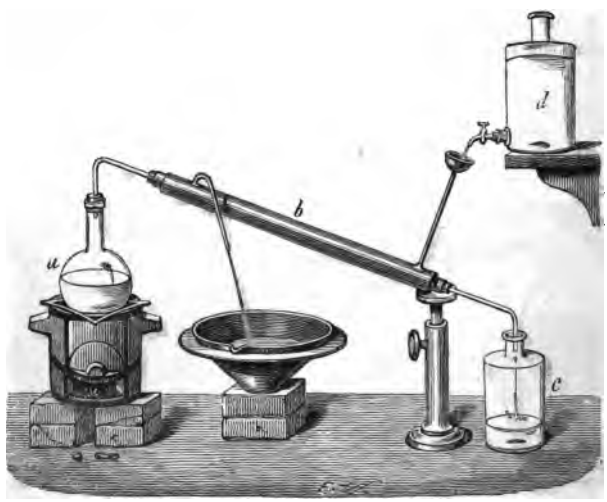


Fig. 35.

through a tube which is surrounded by another, *b*, which is kept constantly filled with cold water from *d*.

An apparatus for distillation on a larger scale, in which the condensation is effected in a spiral pipe called a *worm*, is shown in *fig.* 36.

RETORTS of various forms are shown in *figs.* 37, 38, 39, 40.

66. GAS APPARATUS. Gases are generally obtained by the decomposition of liquids or solids, either by heat or by chemical

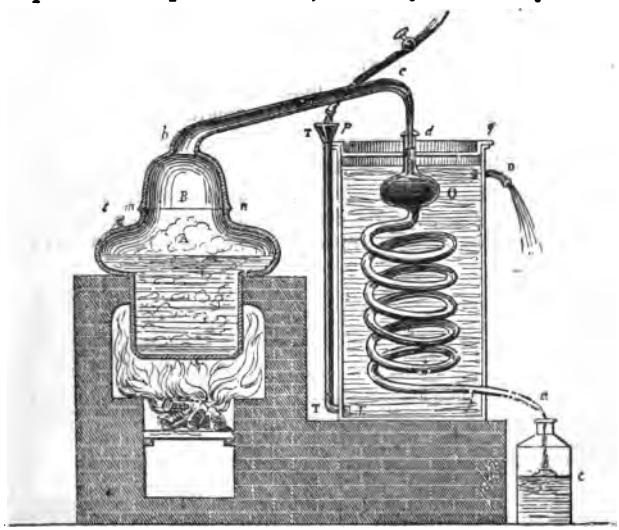


Fig. 36.

reagents. When the gas has been obtained, it is collected in a glass vessel of cylindrical form, which is immersed mouth downwards in a cistern of liquid, usually water or mercury.

Fig. 37.

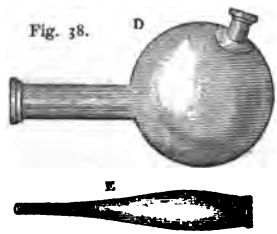


Fig. 40.

Fig. 39.

This vessel being filled with the liquid, is raised with its mouth still submerged, so that it still remains filled, the liquid being supported in it by the pressure of the atmosphere on the surface of the liquid in the cistern.* If the gas be then introduced under the mouth of this vessel, it will rise in bubbles in the vessel, and will collect above the liquid, expelling the latter from the space it occupies.

* See Nat. Phil. for Schools. Chap. x.

67. THE PNEUMATIC TROUGH with its accessories, constructed on this principle, consists of a wooden, stone, or iron cistern, nearly filled with water or mercury, in which a shelf pierced with a series of holes is fixed a little below the surface of the liquid. Glass receivers, being previously filled with the liquid, are placed mouth downwards over the holes upon the shelf. The gas generated in an adjacent apparatus is conducted by a bent tube, and disengaged under the mouth of the receiver, into which it ascends in bubbles, expelling the liquid which previously filled it.

Such an apparatus containing water is shown in section in *fig.* 41, the gas being supposed to be generated by the heat of a furnace applied to a retort, and to be conducted from the retort to the receiver by the bent tube shown in the figure.

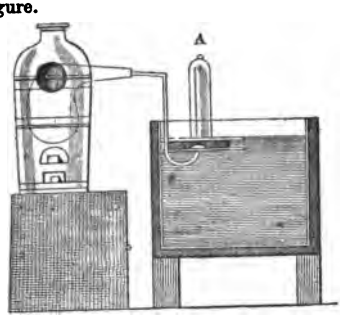


Fig. 41.

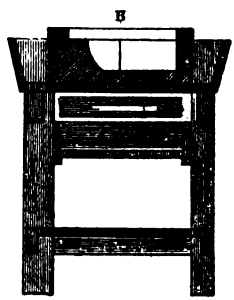


Fig. 42.

When the gas absorbs or decomposes water, mercury is used, and the trough is formed on a smaller scale, as shown in vertical section in *fig.* 42, and in plan in *fig.* 43.

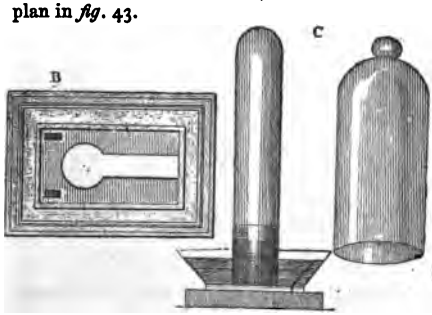


Fig. 43. Fig. 45.

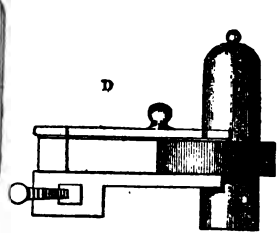


Fig. 44. Fig. 46.

A glass receiver is shown separately in *fig.* 44. When it is required to transport a receiver filled with gas from one place to another, or to retain it apart from the trough, a dish, *fig.* 45, is placed under it, containing sufficient water or mercury to cover the mouth and prevent the escape of the gas.

An arrangement for supporting a gas receiver steadily in an inverted position is shown in *fig.* 46.

TRANSFER TUBES of different forms are shown in *figs.* 47, 48.

68. SAFETY TUBES adapted to confine the gas in a receiver or other vessel, until its pressure exceeds that of a column of liquid filling the tube to the level of the cup, are shown in various forms in *figs.* 49, 50, 51, 52. These are sometimes called *Welter's tubes*, from their inventor.

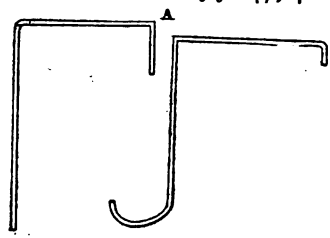


Fig. 47. Fig. 48.

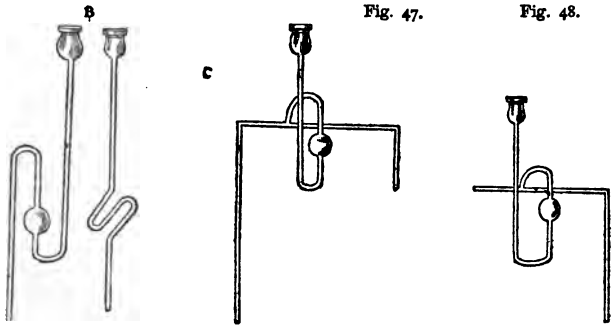
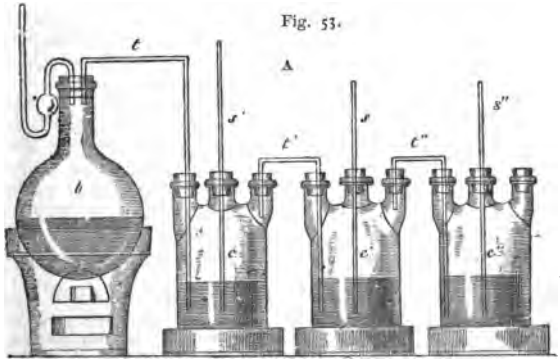


Fig. 49. Fig. 50. Fig. 51. Fig. 52.

69. GAS WASHERS.—WOLF'S APPARATUS. When gases are evolved by physical or chemical agents from liquids or solids, they

Fig. 53.



are seldom pure. To purify them they are transmitted through a series of liquids, which have the property of removing their impurities without absorbing or otherwise affecting the gas.

The form of apparatus used for this purpose, consisting of a series of tubulated flasks, each containing an absorbing liquid, is shown in *fig.* 53, where *b* is the

flask in which the gas is generated, with a safety tube, *t*, *t'*, *t''*, transfer tubes, *s*, *s'*, *s''*, safety tubes. A similar arrangement supplied with Welter's tubes is shown in *fig.* 54.

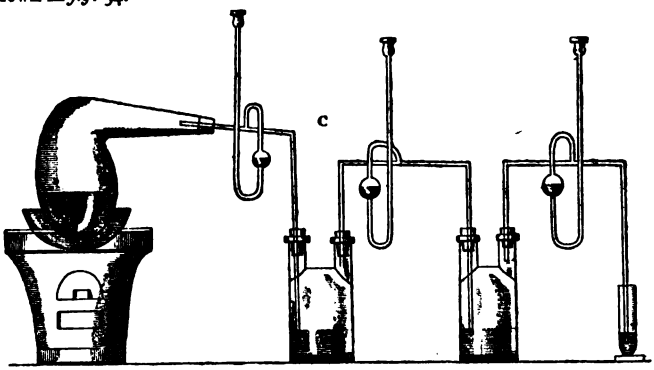


Fig. 54.

70. When gases are evolved in an aqueous solution, or passed through one in the process of washing, they often absorb water, of which they require to be disembarrassed. This is accomplished by transmitting them through some body having a strong affinity for water, without having any affinity for the gas.

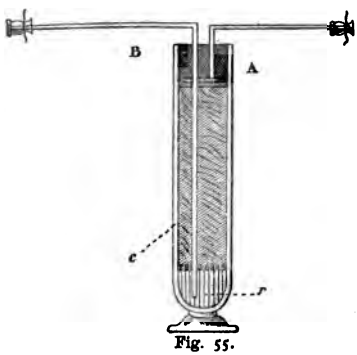


Fig. 55.

The substances most commonly used for this purpose are chloride of calcium (sometimes improperly called chloride of lime), and concentrated sulphuric acid.

When the former is used, it is broken in small pieces and deposited in a glass tube or other convenient vessel, through which the gas to be dried can be readily passed. Its moisture will then be completely absorbed, and it will escape dry.

If sulphuric acid be used, fragments of pumice stone well soaked with it are applied in the same manner.

These absorbents are deposited in glass tubes, either straight or U shaped. A test glass is sometimes used, as shown in *fig.* 55. The part *c* contains the absorbent; *r* is the receiver of the liquid. The gas enters the bottom by the rectangular tube B, and escapes from the top after passing through the absorbent by the other rectangular tube A.

A straight drying tube filled with the absorbent is shown at D, *fig.* 56, as applied to Marsh's arsenic apparatus which will be described hereafter.

71. GASHOLDERS are vessels in which gases can be kept for use in considerable quantities.

One of the most convenient is that contrived by Pepys, consisting of a copper cylindrical vessel B, *fig.* 57, surmounted by a cistern *a*, with which it communicates by two pipes with stopcocks, one of which extends nearly to the bottom

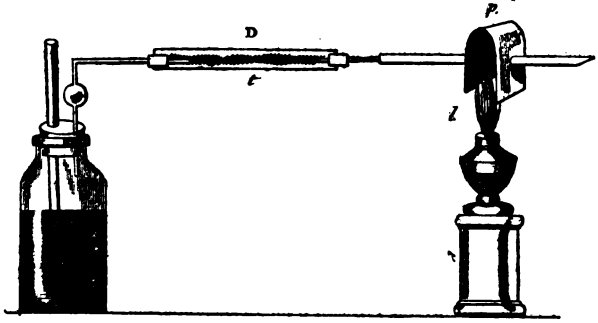


Fig. 56.

of B; a short pipe *c*, of large calibre, bent upwards, issues from the lower part. This can be at pleasure closed by a water-tight stopper. A glass water-gauge is inserted at top and bottom of B, to indicate the level of the water within. The level of the column of water in this gauge will necessarily correspond with that of the water within. The pipe *c* being plugged, and the stopcocks in the

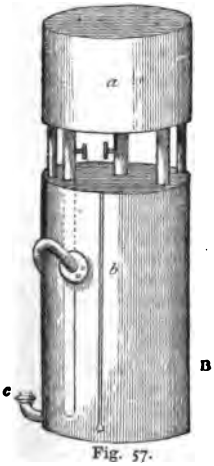


Fig. 57.

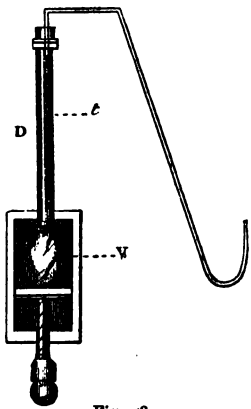


Fig. 58.

connecting-pipes both opened, the apparatus may be completely filled by pouring water in sufficient quantity into the cistern *a*. While the water descends into B, through the long pipe, the air will escape through the short one. When the entire apparatus is filled with water, the stopcocks are both closed, and the stopper taken out of the pipe *c*. The pressure of the atmosphere will prevent the escape of the water from *c*, so long as the apparatus is air-tight.

Now, to fill the gasholder B, with the gas which it is desired to keep, the bent end of a transfer tube (such as *fig.* 48) is introduced through the pipe *c*, the

other end being connected with the reservoir or apparatus in which the gas is generated, or from which it can be forced by pressure. It will then rise in bubbles through the water in B, and collecting in the upper part, will force the water out through *c*, and this will continue until so much of the holder is filled with gas as may be thought necessary.

When it is desired to transfer any quantity of this gas to any other vessel or receiver, the stopcock in the long tube is opened, and the gas in B is then subject to the pressure of the column of water extending from the surface of the water in B, to the surface of water in *a*. A cock provided for the purpose near the top of B (not shown in the figure) is then opened, and being connected with the vessel intended to receive the gas, the gas is forced through the cock into this vessel by the pressure of the water, and it continues thus to pass until the required quantity has been transferred.

72. THE TRANSFER OF GASES is sometimes effected by the apparatus shown in *fig.* 58, consisting of a glass tube D, or receiver of large calibre, connected with a membranous bag V, filled with mercury, and capable of being compressed by a screw, so that the mercury is forced up into D, which it fills. When the screw is lowered, and the bag released from the compression, the mercury falls, leaving a vacuum into which the gas is drawn by suction through the transfer tube.

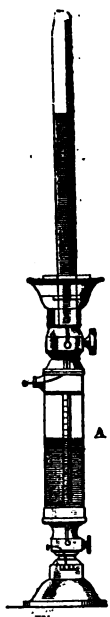


Fig. 59.

Fig. 60.

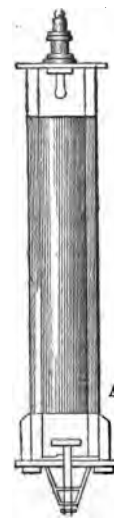


Fig. 61.

73. Eudiometers are instruments originally employed for determining the purity of atmospheric air, or more strictly speaking, for determining the proportion of oxygen it contains, but now used for the analysis of other gases and gaseous mixtures.

The analysis of the air is usually accomplished by ascertaining the quantity of hydrogen which will combine with the oxygen present in exploding. The principle involved in this will be more fully explained hereafter. Different forms of explosion-eudiometers are shown in *figs.* 59, 60, 61. These instruments usually consist of a very thick and stout glass tube of large calibre, within which the explosive mixture is contained, and which is provided with means by which an electric spark can be produced within it, so as to excite the explosion. Two small brass knobs, connected by wires with the electric machine or Leyden jar effect this.

LIEBIG'S BULBS, for effecting the absorption of carbonic acid and other gases by transmitting them through solutions for which they have a strong affinity, are shown in *fig.* 61 A.

74. FURNACES AND CRUCIBLES. When it is considered how important an agent heat is in the development of chemical

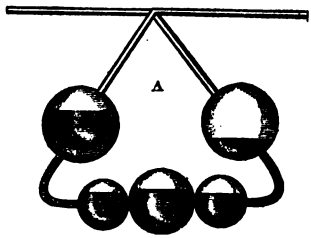


Fig. 61 A.

Fig. 62.

phenomena, it will not be surprising that furnaces of various forms, sizes, and material, with crucibles and other accessories, enter largely into the furniture of the laboratory.

Fig. 62 is a small earthen furnace much used.

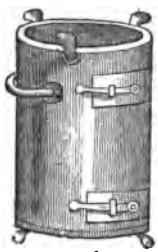


Fig. 63.

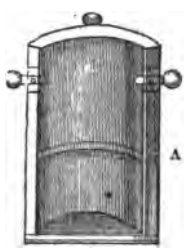


Fig. 64.

Figs. 63, 64 are furnaces of cast iron for evaporation.

Fig. 65 is a reverberatory furnace, shown in section in *fig.* 66, the grate in

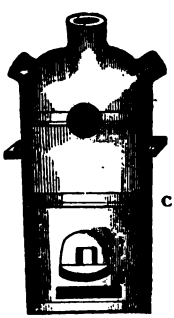


Fig. 65.

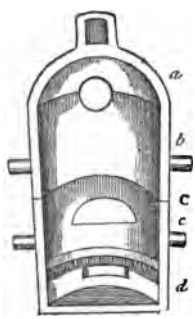


Fig. 66.

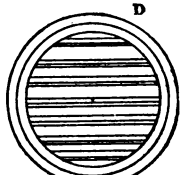


Fig. 67.

fig. 67, *a* the chimney, *b* the space for the object to be heated, *c* the fireplace, *d* the ashpit.

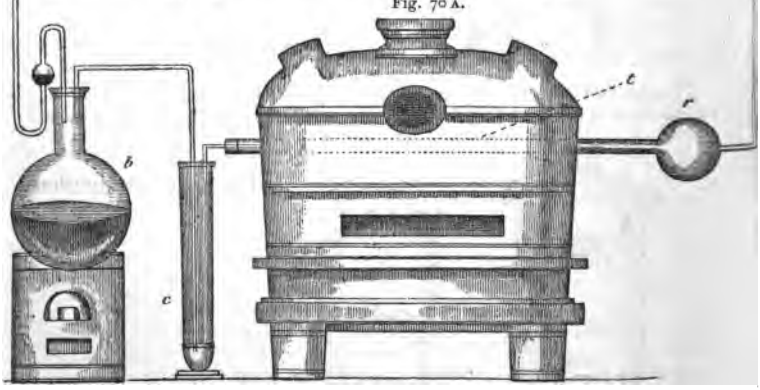
Fig. 68 a furnace of cupellation for assay; v the part to receive the semi-cylindrical earthen piece, *fig.* 69, called the *muffle*, within which the crucibles and cupels are placed. P, H, K, *fig.* 70, are crucibles, G a cupel or bone-earth cup for the reception of the metals, and R are tongs for withdrawing the crucibles and cupels from the furnace, S is an earthen support for a cupel.

Fig. 69.

Fig. 68.

Fig. 70.

Fig. 70 A.

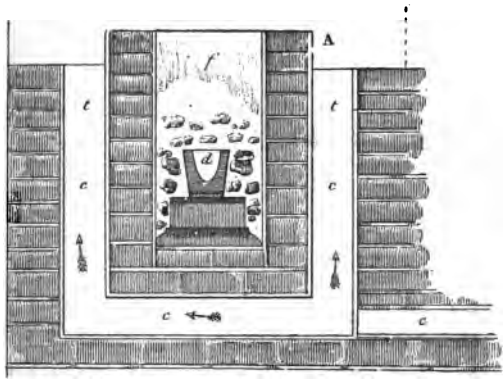


A common arrangement for transmitting gas through a tube heated in a furnace, is shown in *fig.* 70 A.

75. FORGES are used in the laboratory, for the decomposition of salts and metallic oxides. The process consists in stimulating the combustion of the fuel, by forcing through it a current of air, by means of powerful bellows. The section of a forge is shown in *fig.* 71, where *c* is the passage through which the blast-

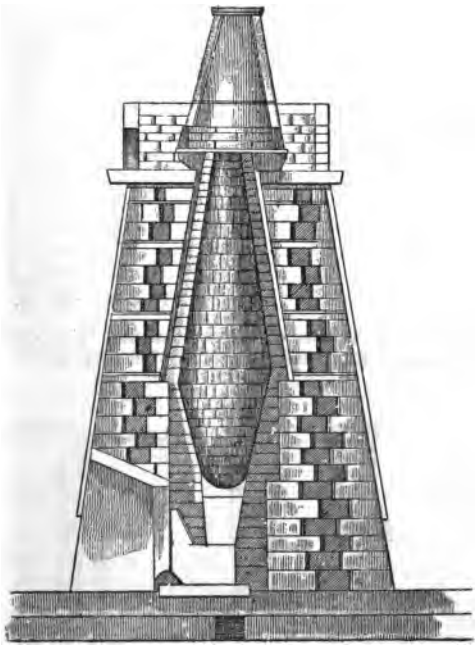
pipe of the bellows impels the air, and *t*, *t*, those by which it is admitted to the fuel, *f* is the fireplace containing the crucible *d*.

Fig. 71.



76. A BLAST-FURNACE, shown in section in *fig.* 72, is a forge upon a large

Fig. 72.



scale, which is worked by a blowing engine, usually driven by a steam-engine. Iron ores are reduced in these vast forges, yielding the iron in the metallic state.

77. THE BLOWPIPE is an instrument of frequent application. It has been constructed in various forms.

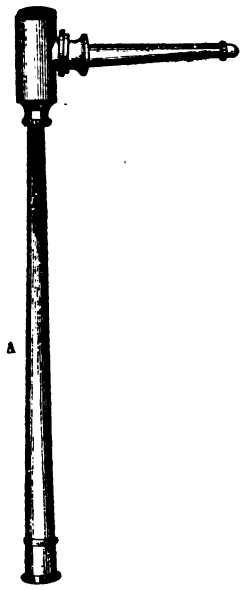
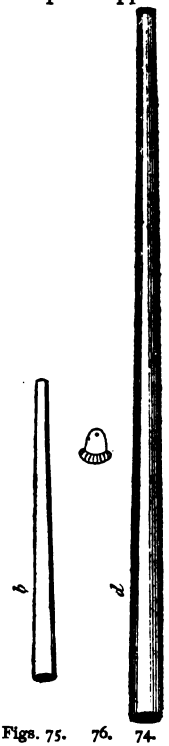


Fig. 73.



Figs. 75. 76. 74.

The most convenient is that of Pepys, consisting of a pipe A, *fig.* 73, a reservoir to retain moisture, and a blastpipe. The parts are shown separated

Fig. 78.

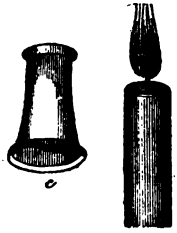


Fig. 77.

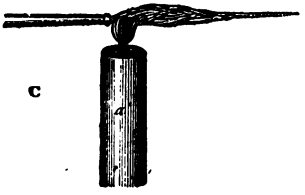


Fig. 79.

and on a larger scale in the succeeding figures. *Fig.* 74 is the principal pipe, 75 the blastpipe, 76 a nipple of platinum to attach to it, 77 the ivory mouthpiece attached to the larger end of *fig.* 74, 78 the reservoir to condense the

moisture of the breath, and 79 the flame as affected by the blast proceeding from the platinum nipple.

Fig. 80 are pincers with platinum points, infusible in the flame, to hold objects exposed to its action.

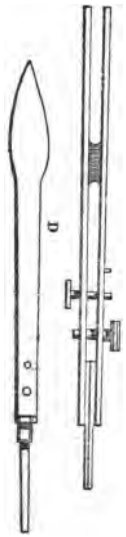


Fig. 80.

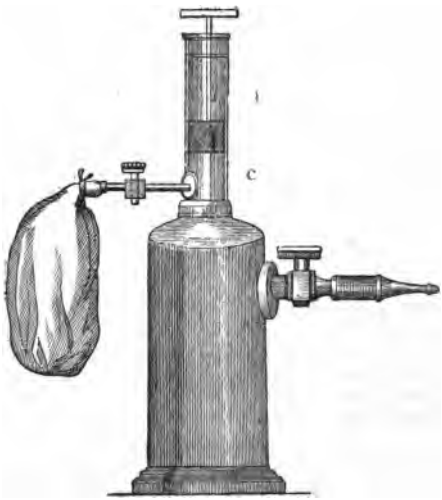


Fig. 81.

78. NEWMAN'S COMPRESSION BLOWPIPE is shown in *fig.* 81. In this the air is forced out through the lateral nozzle, by the pressure of a plunger in the cylinder, over the gas or air holder. If gases are used, they are introduced through a pipe in the side of the cylinder, from a bladder.

*** In the succeeding part of this volume the following abbreviations have been adopted:—S G, specific gravity, referred to water as the unit for solids and liquids, and to air for gases; see Hand Book Nat. Phil., Hydrostatics, Chap. 1.—E, equivalent; = equals; + addition; — subtraction; and × multiplication.

CHAPTER VI.

OXYGEN.—HYDROGEN.—NITROGEN.—AMMONIA.

OXYGEN.

79. OXYGEN is incomparably the largest and most important constituent of the material world. It constitutes one-fifth of the atmosphere, eight-ninths of the water, and enters, as a component, in a greater or less proportion, into all the forms of earth and rock, as well as nearly all the mineral. Its affinities for the metals are universal, and scarcely less so for the metalloids. It is

calculated, aproximately, that this gas in its various combined states, forms about one-third of the matter comprising the globe.

Oxygen is, when uncombined, a permanent gas, with SG = 1·1056, and E = 8. It has never been liquefied. When briskly compressed, its temperature rises to 400°. Its presence is essential to the maintenance of animal life and of combustion, in consequence of which it is called *vital air* and a *supporter of combustion*. It is not, itself combustible; but causes combustion, under suitable conditions, in a class of bodies called *combustibles*.

Its properties are considerably modified by electricity. Where a series of electric charges have been transmitted through it, its affinities are rendered more active, and it acquires a phosphoric odour. In this state it has been called *ozone*, or electrified oxygen.

80. PREPARATION. Never existing naturally unmixed or uncombined, it must be prepared by artificial processes.

The most convenient method of preparation is, by decomposing a salt, called the *chlorate of potash*, by heat. This salt is a compound of chloric acid ClO_5, and potash KO, and is therefore KO, ClO_5. By heating it, both of its components are decomposed, the 6 equivalents of oxygen being liberated, and the chlorine Cl and potassium K uniting to form the compound called *chloride of potassium* KCl. The change is thus represented :—

$$KO,ClO_5 = KCl + O_6.$$

About 39 per cent. of the chlorate is thus liberated as the gas oxygen. The apparatus for this process is shown in *fig.* 82. The salt in a glass retort is placed over a lamp, and the gas evolved is collected in a receiver over water.

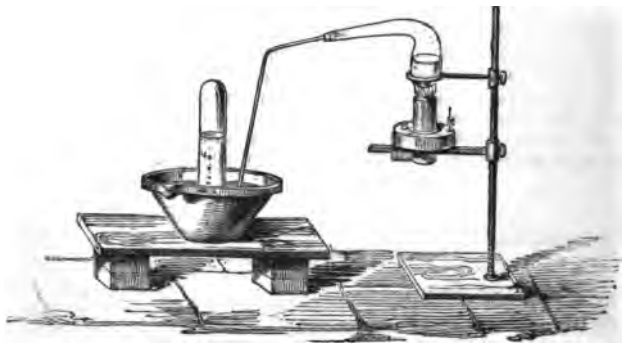


Fig. 82.

81. EXPERIMENTS WITH OXYGEN. Combustible bodies burn with extraordinary splendour in oxygen. Such experiments are performed in a glass jar or receiver, filled with the gas and closed by a stopper. If a candle or match be lighted and blown out, leaving the wick red, it will be instantly relighted when plunged in such a jar, and will burn with much more splendour than in the air. If sulphur or phosphorus well dried, be placed in a capsule, and

being set fire to, be plunged in such a jar, *fig* 83, it will burn with great brilliancy. The light of the phosphorus will be insupportable. A spiral steel-wire, *fig*. 84, heated to redness at the extremity, will burn, scattering brilliant sparks.

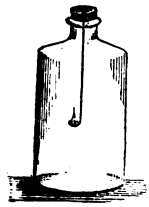


Fig. 83.

Fig. 84.

In all these cases the combustible body, in burning enters into combination with the oxygen, producing, in the case of sulphur and phosphorus, sulphurous and phosphoric acids, and in the case of the wire, oxide of iron. The heat, which is developed in these combinations, is so intense as to render the compound produced incandescent, and thence arise the luminous phenomena which characterise the combustion. How chemical combination developes heat, which it does in most cases, has not been explained.

HYDROGEN.

82. HYDROGEN, which takes its name from being one of the constituents of water, is the lightest body known, whether simple or compound. Its SG = 0·0692, being, therefore, more than 14 times lighter than common air. This levity is so great that it may be easily passed from one receiver to another, by merely holding that which contains the gas under the other, *fig*. 85. Its E = 1.

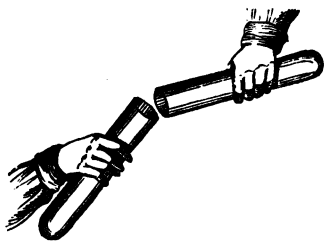


Fig. 85.

Its tenuity is so extreme, that it easily penetrates bodies (such, for example, as paper), which are almost impermeable by other gases. It is highly combustible, burning with a bluish and faintly luminous flame. It is scarcely soluble in water; but, when required pure, should nevertheless be collected over mercury, since water generally holds other gases in solution, with which it would become mixed.

83. Hydrogen and oxygen combined, equivalent for equivalent, form water, the composition of which is, therefore, HO.

This is proved experimentally by introducing the two gases, in the proportion of one measure of oxygen to two of hydrogen (§ 18), into an eudiometer (§ 73), and transmitting an electric spark through the mixture, when an explosion will ensue, the gases will disappear, and will be replaced by aqueous vapour, which will be immediately condensed and converted into water, *fig*. 86.

84. Conversely, water, being decomposed, is converted into oxygen and hydrogen, in the proportion of one measure of the former to two of the latter.

This is demonstrated by applying the two poles of a voltaic battery to water, when decomposition will ensue, the oxygen being evolved from the point of the

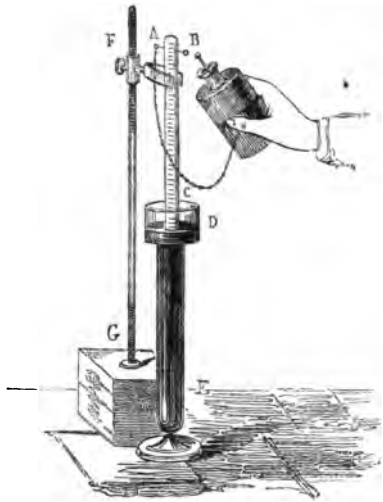


Fig. 86.

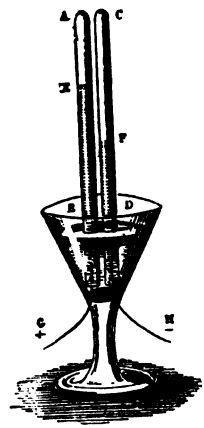


Fig. 87.

positive, and the hydrogen from that of the negative, wire. The two gases being received in graduated tubes, *fig.* 87, it will be found that the volume of hydrogen will be twice that of the oxygen.

85. Since water = HO, it follows, therefore, that 9 parts of water consist of 1 of hydrogen combined with 8 of oxygen, for an equivalent of oxygen = 8, and one of hydrogen = 1.

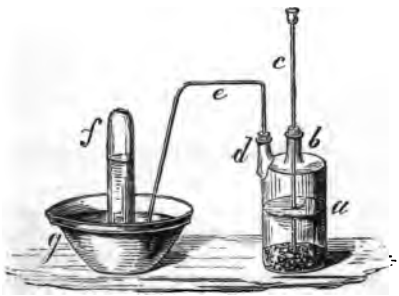


Fig. 88.

86. PREPARATION. Hydrogen is prepared by the decomposition of water, and the most convenient process is the following:—

Let granules of pure zinc be immersed in acidulated water in a tubulated bottle *a*, *fig.* 88. The water will be decomposed, its oxygen combining with the zinc, and its hydrogen being liberated. The oxide of zinc thus formed will instantly combine with the acid to form a salt of zinc, which will remain in solution, or will be deposited. Meanwhile, the hydrogen collecting in the flask may be transferred in the usual manner to a receiver, *f*, over water.

The effects produced may be thus stated, the water being supposed to be acidulated with hydrated sulphuric acid HO, SO_3 :—

$$HO,SO_3 + Zn = ZnO,SO_3 + H.$$

The salt produced in this case is sulphate of zinc, ZnO, SO_3.

87. USES. Hydrogen is of great use in the laboratory to *reduce* metallic oxides; that is, to decompose them, so as to obtain their metallic bases in a separate state. It also serves for a like reduction of metallic chlorides and sulphurets.

Its great levity renders it very effective for filling balloons.*

88. WATER, which, chemically considered, is the protoxide of hydrogen, HO, is a perfectly neutral body, possessing neither basic nor acid properties. It does not redden litmus, nor restore its colour when reddened. It is decomposed by bodies which have a strong affinity for oxygen, and combines with many bodies in definite proportions, producing a large and important class of compounds, called *hydrates*. When thus united, it seldom modifies their peculiar properties; so that such compounds, as well as aqueous solutions, present most convenient means of investigating their properties. In some cases, however, water produces important modifications of the bodies with which it combines. Thus, certain salts, when dissolved in water, are decomposed, one of their constituents being insoluble. Examples of this are presented by nitrate of bismuth and stearate of potash.

89. OXYGENATED WATER, or binoxide of hydrogen, is a combination of one equivalent of hydrogen with two of oxygen, HO_2.

This compound is important, as having first shown that bodies may produce important chemical effects by their mere presence, without either imparting to or taking away from the body acted on, any material principle.

It is a liquid without colour or odour, having a taste resembling that of certain metallic salts. It whitens the skin, and discolours litmus. Its SG = 1·452. It is decomposed by the mere presence of certain bodies, such as silver, platinum, carbon, lead, bismuth, the alkaline hydrates, and by animal fibrine.

90. Whenever pure hydrogen is inflamed in the air the product of the combination is water, formed by the combination of the gas with the oxygen of the air, in the proportion of 1 part by weight of the gas to 8 of the oxygen, or what is the same, 2 volumes of the gas to 1 volume of oxygen.

If a glass jar be held over a jet of inflamed hydrogen, *fig.* 89, the aqueous vapour formed by the combination of the gas with the oxygen of the air will be condensed on the inside of it, and collecting there, will soon be seen trickling down, and may be received in drops by a dish placed under it.

91. Hydrogen, though combustible itself, does not support combustion. An ignited body immersed in it is instantly extinguished.

* See H. B. Nat. Phil. Pneumatics. § 245.

92. If hydrogen and oxygen, in the proportion of two measures of the former to one of the latter, be mixed together, they will retain their gaseous state without combining. They will be merely interfused like the gases which form the atmosphere. But upon the application of any determining agent, such as a spark of fire or of electricity, combination attended with an enormous development of heat will take place. The gases will be suddenly converted into steam, with an explosion produced by the expansion of the vapour thus generated at the high temperature imparted to it by the heat developed. The vapour thus produced, being condensed by the cold of the surrounding surfaces, will be reduced to water.

The manner in which this experiment is performed has been already explained (§ 83).

93. THE OXYHYDROGEN BLOWPIPE, an instrument of great use in chemistry and the arts, is constructed on this principle: Oxygen and hydrogen are

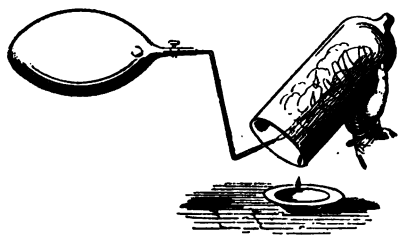


Fig. 89.

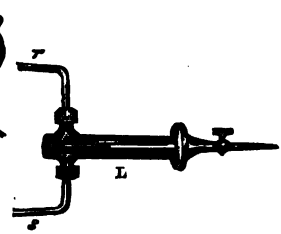


Fig. 90.

conducted in the proper proportion from two reservoirs or gasholders by pipes, *r*, *s*, *fig.* 90, to a common nozzle L, from which they issue mixed together. The jet being ignited a flame is produced, which has a temperature more elevated than that of any source of heat hitherto produced artificially, except that of charcoal points rendered incandescent by a voltaic current.

The flame of the blowpipe burns with facility most of the common metals, such as steel, or iron, antimony, copper, and so on, converting them into their oxides.

94. THE DRUMMOND LIGHT is produced by projecting the flame of such a blowpipe upon a ball of lime, which it renders so brilliantly incandescent that the eye can scarcely support it.

95. Hydrogen has a high refracting power, which is common to it and all transparent combustibles.

96. If a lighted jet of hydrogen be introduced into a glass tube, open at both ends and held vertically, a peculiar musical sound will be produced. This phenomenon is generally explained by the supposition of a rapid succession of explosions produced by the combustion of the gas within the tube.

NITROGEN.

97. NITROGEN or azote is a permanent gas without colour, taste or odour. It is neither combustible nor a supporter of combustion. It is irrespirable, but only so from the absence of oxygen, and

not from any deleterious property. It is characterised by negative rather than positive qualities. Its SG=0·972, and E=14. It is completely neutral to the colour tests § §32, 34.

Atmospheric air is a mixture of 79·2 volumes of nitrogen with 20·8 of oxygen. In relation to respiration the use of nitrogen as a constituent seems to be merely to dilute the oxygen. An atmosphere containing a greater proportion of oxygen would be too strong, and one containing a less proportion too weak for healthy respiration.

98. PREPARATION. This gas is most conveniently prepared by depriving air of its oxygen. This is accomplished by burning, under a receiver filled with air, any combustible which forms with oxygen a compound not gaseous. Phos-

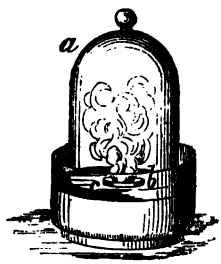


Fig. 91.

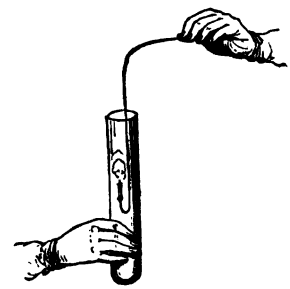


Fig. 92.

phorus is generally selected. A piece of that substance well dried is burned in a capsule *b*, within a receiver *a*, inverted over water *c*, *fig.* 91. The phosphorus combining with the oxygen forms phosphoric acid, which is dissolved in the water, and the nitrogen remains separate. The water rises in the receiver occupying the place deserted by the oxygen, that is, a little more than one-fifth of the capacity of the vessel.

99. The name *nitrogen* was given to this gas because it constitutes a part of nitre or saltpetre. Foreign chemists generally call it *azote*, from a Greek term signifying privation of life.

If a test-glass be filled with nitrogen, a candle immersed in it is immediately extinguished, *fig.* 92. An animal which breathes in it dies.

It is less soluble than oxygen in water, which only dissolves the 60th part of its volume of the gas. Although it combines directly with only a few bodies, its compounds are characterised by remarkable properties very different from the merely negative qualities of the gas. It enters largely into the composition of the organic world.

100. COMBUSTION. Common combustion consists in the combination of a combustible with the oxygen of the atmosphere. In this process the oxygen alone is absorbed, the nitrogen not being affected. Since the compounds resulting from such combustion

are themselves incombustible, they require to be removed from the combustible as fast as they are produced. Hence a draft of air is necessary through the burning matter. But the air thus propelled is not alone necessary to carry away the products of combustion, but also to supply fresh oxygen to sustain the combustion of that part of the combustible still unburnt.

The state of subdivision of combustibles exercises an important effect on combustion. Thus iron, charcoal, and sulphur, which will in general burn only when raised to a high temperature, will inflame at common temperatures when exposed in a state of comminution to the air. Bodies in this state are said to be *pyrophoric*, their inflammation being ascribed to the air absorbed and condensed in their pores.

The combustion of an inflamed body, a candle for example, is continued when once begun, because the heat developed by the part which burns is imparted to the contiguous parts and raises them to a temperature sufficiently high to cause their combustion. On the contrary the combustion is discontinued when any cause cools the adjacent parts. A candle is extinguished by a blast of cold air, because it carries away the heated gases of the flame before they have time to impart heat to the adjacent part of the wick.

101. FLAME is nothing more than gas *white hot*. If it be cooled it will cease to be luminous.

102. THE SAFETY LAMP of Sir H. Davy is constructed on this principle. Coal miners being liable in the workings of mines to be surrounded with an explosive atmosphere, from which terrible disasters have from time to time occurred by reason of their lamp setting fire to the gaseous mixture, the safety lamp was contrived to afford at once a warning of the danger and a protection against it. The apparatus consists of a lamp surrounded by a cylinder of fine metallic gauze, *fig.* 93. When it is carried into an explosive atmosphere, a slight detonation takes place within the wire gauze, the entire quantity of gas within being inflamed. The flame thus produced however is extinguished in passing through the wire gauze, to which it imparts so much of its heat that the gas of which it is composed ceases to be incandescent, and is consequently incapable of inflaming the explosive gas exterior to it after passing through the meshes of the gauze. The wire gauze cylinder is shown in *fig.* 94, a section of the lamp in *fig.* 95, and other parts in *figs.* 96, 97. A platinum wire placed in the interior of the lamp becomes incandescent, when the mixed gases burn within the lamp, and aids in giving light.

103. THE ILLUMINATING POWER of flame depends on the nature of the combustible. When the products of combustion are merely gaseous, the illumination is feeble, such are, for example, the flames of hydrogen, carbonic oxide, and alcohol. But when solid molecules are found in it, they become intensely incandescent, and give whiteness to the flame. Hence arises the intense light of the flame of phosporus and zinc. The flames of gas used for illumination, stearine or wax candles, and oil lamps, are brilliant and white, because they contain molecules of incandescent carbon.

The temperature of a flame is quite distinct from and independent of its illuminating power. The flame of hydrogen, which is but faintly luminous, has an intense heating power.

104. THE COMPOUNDS OF NITROGEN AND OXYGEN have been already stated § 16.

105. NITRIC ACID, the most important of these compounds, is usually found combined with water as an hydrate, but may be obtained in the anhydrous state by decomposing nitrate of silver completely deprived of water, AgO, NO_5, by a current of perfectly dry chlorine gas. The chlorine combines with the

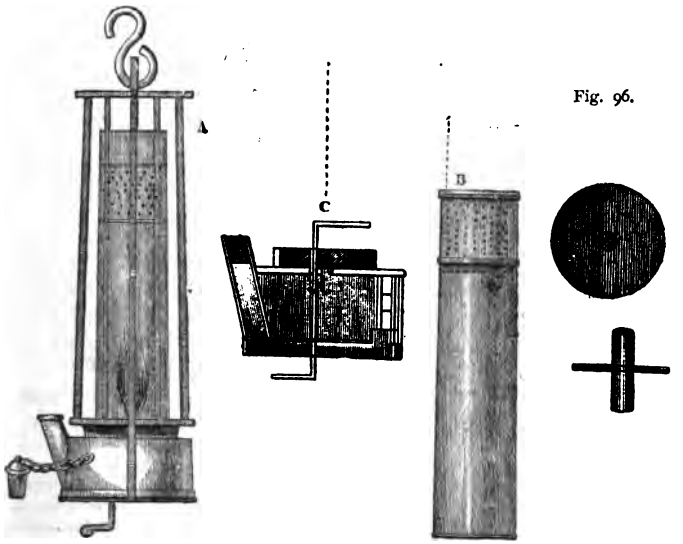


Fig. 96.

Fig. 93. Fig. 95. Fig. 94. Fig. 97.

silver, the oxygen of the oxide is set free, and the nitric acid, NO_5, perfectly anhydrous, is separated as a white substance crystallised in forms derived from the right prism with a rhomboidal base. It fuses at 86° and boils at 113°. If heated still more it is decomposed, being resolved into nitrous oxide and oxygen—

$$NO_5 = NO_4 + O.$$

The operation must be conducted out of contact with cork, caoutchouc, or other organic matter upon which the acid would exercise a strong action.

106. HYDRATED NITRIC ACID, NO_5, HO, is instantly produced by the contact of the anhydrous acid with water. This, which in fact is the only state in which its property of acidity is really manifested, is a colourless liquid, highly corrosive, fuming in air, and a strong poison. It rapidly destroys all organic bodies. The smallest drop applied to the skin disorganises it, leaving a yellow stain. It imparts a like colour to all organic compounds, and this property is utilised in the arts to dye feathers, silk, and other bodies; it serves also as a test to detect small quantities of nitric acid in analyses.

At 18° its SG = 1·510. It boils at 186·8°, and is congealed into a butter-like mass at −58°.

107. The tests of acidity not being capable of application to the compound NO_5, no proof exists that it is an acid at all. When hydrated the acid properties are strongly manifested. This circumstance has been hitherto explained by the supposition that the combination of NO_5 with water, renders the application of the acid tests possible, and thus developes the acid character of the anhydrous compound.

108. Lately however another view of the phenomenon has been advanced, in which the compound NO_5 in combining with an equivalent of water HO decomposes the latter, combining with its oxygen to form the new compound NO_6. This latter enters into combination with the hydrogen of the water, which gives it acidity, just as hydrogen gives acidity to chlorine, bromine, iodine, &c., in the production of the hydracids of those elements.

This is an example of the new system already mentioned, by which it is proposed to reduce oxacids to hydracids, § 41. *note*, page 11. In this system therefore hydrated nitric acid would be written H, NO_6, where NO_6 is an hypothetical compound which plays the part of a radical and combines like a simple element with hydrogen, which is regarded here as the acidifying agent.

109. The hydrate NO_5, HO manifests an affinity for water. Mixed with water an elevation of temperature is produced, due to combination of the hydrate with water.

If this hydrate be kept boiling for some time, it will be partially decomposed, evolving nitrous acid and oxygen; the residue will of course contain an increased proportion of water. According as the acid is decomposed its boiling point rises, and at length becomes stationary at 253°. At this point the acid is reduced to an hydrate, including 4 equivalents of water, NO_5, 4HO. When a more dilute solution is distilled, the excess of water is evaporated and the acid is soon reduced to this hydrate.

It appears therefore that highly concentrated acid is rendered more dilute, while very dilute acid is rendered more concentrated by distillation.

110. ACTION ON METALS. This acid dissolves almost all the metals. It first oxidises them and then converts their oxides into nitrates. All the nitrates being soluble, the metals are thus ultimately dissolved.

As examples of this reaction we give here the formulæ expressing the effect of the acid on copper and silver.

$$4NO_5,HO + 3Cu = \overbrace{3CuO,NO_5}^{\text{Nitrate of copper.}} + \overbrace{NO_2}^{\text{Nitric oxide.}} + 4HO.$$

$$4NO_5,HO + 3Ag = \overbrace{3AgO,NO_5}^{\text{Nitrate of silver.}} + NO_2 + 4HO.$$

It appears therefore that in the reaction 3 equivalents of oxygen combine with the metal to form its oxide, which combines with as many equivalents of

the acid to form the soluble nitrate, while 1 equivalent of nitric oxide is dismissed as gas, and 4 equivalents of water aid in dissolving the nitrate.

111. It might appear that the hydrate NO_5, HO would be a more powerful oxidant than NO_5, 4HO. Such, however, is not the case. Thus, iron, copper, and tin, are actively attacked by NO_5,4HO, but are not at all affected by NO_5,HO.

112. PREPARATION. This acid is usually prepared in the laboratory by heating a mixture of 6 parts of nitre KO,NO_5, with 4 of the sulphuric acid of commerce (vitriol) SO_3,HO, in a glass retort, *fig.* 98, and condensing the vapour in a cold receiver. The result is thus expressed :—

$$\underbrace{KO,NO_5}_{\text{Nitre.}} + \underbrace{2SO_3,HO}_{\text{Sulphuric acid.}} = \underbrace{NO_5,HO}_{\text{Nitric acid.}} + \underbrace{KO,(SO_3)_2HO}_{\text{Bisulphate of potash.}}$$

The sulphuric acid should be poured into the retort, without allowing it to

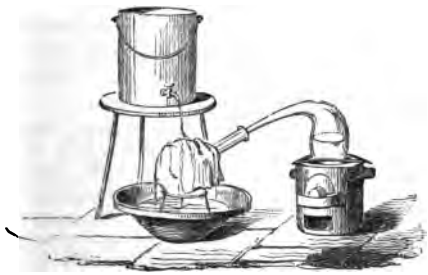


Fig. 98.

Fig. 99.

wet the neck. This is effected by a funnel with a long tube, as shown in *fig.* 99.

113. USES. Owing to its oxidating power, this acid is much used, both in the laboratory and in the arts. It is used in the manufacture of vitriol and oxalic acid, in dyeing, in copper and steel engraving, in assaying, and in the cleansing of metals, and the production of gun-cotton. In chemical analyses it serves for the solution of the metals, most of the oxides, the carbonates, &c. By its oxidating power, it transforms oil of bitter almonds into benzoic acid, camphor into camphoric acid, indigo into indigotic acid, and so on.

114. NITROUS ACID, NO_4, called by the French chemists hyponitric acid, is a yellowish liquid, which crystallises at 15·8°, and boils at 71·6°. Its SG = 1·451. It diffuses, when exposed to the air, a reddish vapour of SG = 1·70, reddens litmus, stains the skin yellow, and disorganises it. It is a powerful oxidant, producing rapidly the oxidation of sulphur and phosphorus. It has no action on the hydracids of chlorine and bromine, but decomposes those of sulphur and iodine.

115. PREPARATION. Nitrate of lead PbO,NO_5, raised to a red heat, is resolved into this acid, with separation of the oxide PbO and 1 equivalent of oxygen :—

$$PbO,\ NO_5 = NO_4 + PbO + O.$$

The salt, which always retains water between its crystals, being well dried, is placed in a stoneware or glass retort, *fig.* 100, the neck of which is well luted into a siphon-formed condenser, which is immersed in a freezing mixture. The acid will be condensed in this as a yellow liquid.

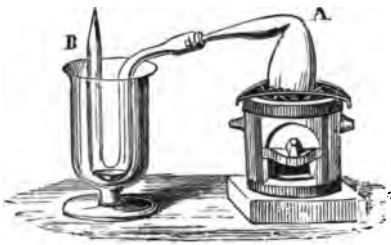


Fig. 100.

116. NITRIC OXIDE, NO_2, otherwise called the binoxide, or deutoxide, of nitrogen, is a colourless gas, very sparingly soluble in water. SG = 1·039. Its taste and smell are unknown; for, the moment it is exposed to the air, it takes up oxygen, and is converted into nitrous acid, in the form of red vapour. It consists, by volume, of 2 volumes of nitrogen, and 2 of oxygen.

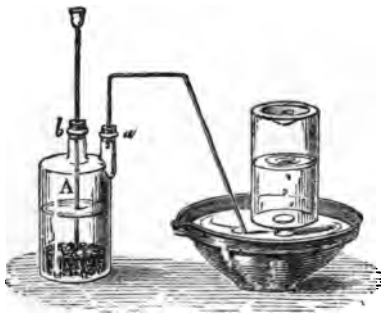


Fig. 101.

117. PREPARATION. This gas is prepared by the action of metals on nitric acid, NO_5, which, by absorbing 3 equivalents of its oxygen, reduce it to nitric oxide. Copper may be conveniently used, the process being effected in an apparatus, *fig.* 101, similar to that used in the preparation of hydrogen. Copper shavings are immersed in dilute nitric acid in the flask, A, having a safety tube, *b*. The gas, as it is evolved, is collected in the usual way, over water. The action may be thus expressed :—

$$\underbrace{4(NO_5,HO)}_{\text{Nitric acid.}} + \underbrace{3Cu}_{\text{Copper.}} = \underbrace{3(CuO,NO_5)}_{\text{Nitrate of copper.}} + \underbrace{NO_2}_{\text{Nitric oxide.}} + \underbrace{4HO}_{\text{Water.}}$$

One equivalent of nitric acid parts with 3 equivalents of oxygen, and is reduced to nitric oxide, while the 3 equivalents of oxygen which it dismisses combine with the 3 equivalents of copper to form 3 equivalents of the oxide of copper, which combine with the remaining equivalents of the nitric acid to form 3 equivalents of the nitrate of copper.

It may be here observed, generally, that the salts of the metallic oxides are, for brevity, called salts of the metals. Thus, in the present case, the salt which is formed is, strictly speaking, the nitrate of the oxide of copper, but is more briefly called the nitrate of copper.

118. NITROUS OXIDE, NO, popularly known as *laughing gas*, is capable of being reduced to a liquid, and even to a solid, by the

combination of pressure and a low temperature. It is without colour or odour, and has a slightly sweetish taste. Its SG = 1·5269. It supports combustion, but not so intensely as oxygen. When respired it produces a sort of momentary intoxication, sometimes exciting laughter, whence it derives its popular name.

Heat resolves it into nitrogen and nitrous acid, thus :—

$$4NO = NO_4 + 3N.$$

Its composition by volumes is, 1 volume of oxygen, combined with 2 of nitrogen. Water dissolves half its volume, and alcohol a volume and a half of this gas.

119. PREPARATION. By heating nitrate of ammonia in a glass retort, that salt is resolved into the protoxide and water, thus :—

$$\underbrace{NH_3, HO, NO_5}_{\text{Nitrate of ammonia.}} = \underbrace{2NO}_{\text{Protoxide.}} + \underbrace{4HO.}_{\text{Water.}}$$

AMMONIA.

120. AMMONIA, NH_3, the only compound of nitrogen and hydrogen, is a colourless gas, having a peculiar pungent and penetrating odour. It is easily liquefied at common temperatures by a pressure of $6\frac{1}{2}$ atmospheres. It is irrespirable, and is scarcely combustible in atmospheric air, but may be readily inflamed in pure oxygen. It is not strictly a permanent gas, since it is liquefied under common pressure by the cold produced by the evaporation of sulphurous acid.

It has strong alkaline properties, turning reddened litmus paper blue, and the syrup of violets green. Being the only gaseous body manifesting such properties, it has been called the "volatile alkali."

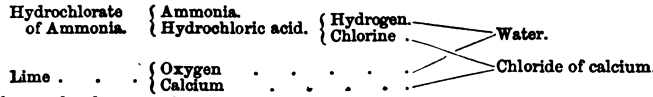
The presence of ammonia may be determined by three tests: 1°, its peculiar odour; 2°, its alkaline property; and 3°, by the white fumes of hydrochlorate of ammonia formed when a glass tube dipped in hydrochloric acid is presented to it.

121. Ammonia is formed by the combination of 2 volumes of nitrogen with 6 of hydrogen. In the combination condensation takes place, the 8 volumes being reduced to 4. The combining volume of this gas is 4.

Of all gaseous bodies ammonia is the most soluble in water. If a test-glass filled with ammonia be inverted over water, the gas will be absorbed so suddenly, that the water will rush up into the glass with almost as much force as if the space within the glass had been a vacuum. So much so that, in making the experiment, the operator should surround the glass with a cloth, to prevent accidents in case of its fracture.

122. This solution of ammonia in water is called *liquid ammonia* and *aqua* or *liquor ammoniæ*. Its SG = 0·85 at 50°. Its point of congelation is about −40°.

123. PREPARATION. This gas is prepared by heating in a mattras, A, *fig.* 102, 1 part of a pulverised salt of ammonia, the hydrochlorate, for example, with 2 parts of quicklime. The salt and the lime are both decomposed, and the ammonia of the former is liberated. The operation may be illustrated thus:—



or it may be thus stated:—

$$\underbrace{NH_3, HCl}_{\text{Hydrochlorate.}} + \underbrace{CaO}_{\text{Lime.}} = NH_3 + \underbrace{CaCl}_{\text{Chloride of calcium.}} + HO.$$

The gas is conducted by the tube B, and collected over mercury in the receiver C.

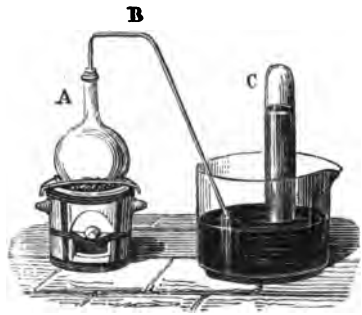


Fig. 102.

CHAPTER VII.

CHLORINE.—BROMINE.—IODINE.—FLUORINE.

CHLORINE.

124. CHLORINE is the only gaseous element which is not colourless and transparent. It is characterised by the peculiar yellowish green colour from which it takes its name; χλωρὸς (chloros), being the Greek name of that particular colour. It has a strong suffocating odour, a caustic taste, SG = 2·44, is incombustible and irrespirable. Drawn into the lungs it produces suffocation, lesions, and spitting of blood.

When reduced by compression to a fifth part of its volume, it is converted into a liquid of the same colour as the gas, with SG = 1·33. This liquid has not been congealed.

This gas is soluble in water, its solubility varying with the temperature, and being greatest at 46·5°, when water absorbs 3 times its volume of the gas. The solubility rapidly decreases with the increase of temperature, the absorption at 122° being 1 volume.

The aqueous solution has nearly the same colour, and manifests

all the properties of the gas. Being more manageable, it is used in preference to the gas in experiments. Being decomposed by the influence of light, it should be kept in a dark place, or the flasks containing it should be coated with black paper.

125. The most important properties of this gas are its bleaching and disinfectant powers.

As a bleaching agent it is extensively used in the manufacture of linen and cotton, and in general wherever it is desired to efface colours of vegetable origin. These colouring matters being composed of carbon, hydrogen, oxygen, and occasionally nitrogen, are strongly acted on. The chlorine seizes upon their hydrogen, forming with it hydrochloric acid, HCl, and the colouring matter being decomposed is bleached. In general, however, the intervention of water in the reaction seems necessary. The water is decomposed, its hydrogen uniting with the chlorine to form hydrochloric acid, and its oxygen oxidating the colouring matter, so as to transform it into a new and generally colourless compound.

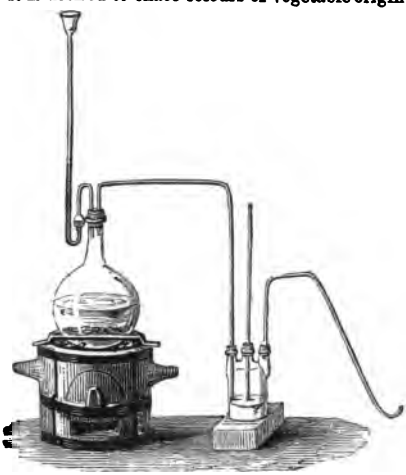


Fig. 103.

126. As a disinfectant it is employed to destroy the miasmata which are disengaged from organic bodies in a state of decomposition. Chlorine destroys, or rather renders innoxious, these effluvia by seizing upon their hydrogen.

PREPARATION. The pulverised peroxide of manganese, MnO_2, is placed in a glass flask, *fig.* 103, upon which hydrochloric acid, HCl, is poured. The peroxide gives up its oxygen to the hydrogen of the acid, producing water, while one-half of the chlorine combines with the manganese to form the protochloride of manganese, and the other half set free passes over by the transfer tube into the gas-washer, and thence to any convenient receiver.

The reaction may be thus illustrated:—

Perox. Mang. . { Mang. . . . . } Protochl. Mang.
{ Oxyg. . . } Water.
Hydrochl. acid . { Hyd. . . }
{ Chlor. { Chlor. . . . . } free.
{ Chlor. . . . . }

or thus—

$$MnO_2 + 2HCl = MnCl + 2HO + Cl.$$

The reaction is promoted by gently heating the flask.

127. **Uses.** Chlorine is much employed in chemical processes and analytical researches. It modifies bodies by separating their hydrogen from them, for which chlorine itself is often substituted. It also determines the phenomena of oxidation. As already stated, it is of great use in bleaching, but for that purpose is applied, not free, but in combination with lime, potash, or soda,

forming compounds called *bleaching chlorides*. As already stated, it is also used in hospitals, sick rooms, and elsewhere, as a disinfectant, but in such case requires to be managed with much precaution.

Chlorine exists in immense quantities in nature, but not in the free state. As already stated, it is combined with sodium in sea or rock-salt. It is also often found in combination with lead, silver, and mercury. Combined with potassium it is a component of ashes, and particularly those of sea-plants.

128. THE COMPOUNDS OF CHLORINE AND OXYGEN at present known are :—

1. Hypochlorous acid . . ClO	4. Chloric acid . . . ClO_5
2. Chlorous acid . . . ClO_3	5. Perchloric acid . . ClO_7
3. Hypochloric acid . . ClO_4	

to which some chemists add chlorochloric acid, $2ClO_5,ClO_3$, and chloroperchloric acid, $2ClO_7$, ClO_3.

Of these the most important are the 1st, 3rd, 4th, and 5th.

129. CHLORIC ACID is a strongly acid liquid, without odour or colour, soluble in all proportions in water. Having little stability, it is a strong oxidating agent, acting promptly on all organic compounds. It inflames alcohol, sets fire to paper, first reddens the tincture of litmus and then destroys it. Litmus paper dipped in it is first reddened, and then bleached.

This compound has but little importance in its separate state; but its salts, and especially the chlorate of potash, KO,ClO_5, have much, being largely consumed in industry, and more particularly in the fabrication of lucifer matches.

130. PERCHLORIC ACID is a solid, soluble in water, strongly acid, and without odour. It volatilises at 284°, resists a dull red heat without decomposition, but a bright red heat resolves it into its two constituents. Hydrosulphuric, sulphurous, and hydrochloric acids, which severally react on chloric acid, have no reaction on perchloric acid.

USES. In chemical experiments this acid is preferable to chloric for precipitating the salts of potash, for the perchlorate of potash is less soluble than the chlorate in cold water.

131. HYPOCHLORIC ACID is a dark-red liquid, which boils at 68°, and is converted into a greenish yellow gas darker than chlorine. It has a disagreeable odour, resembling at once that of caramel and chlorine. Its SG=2·515. It destroys litmus without reddening it. Water at 40° dissolves 20 times its volume of this gas. The solution has an astringent and corrosive taste. It is solidified by a high degree of cold, and converted into a friable crystalline mass. It is very unstable, being destroyed by direct solar light. It is decomposed at 150°. The liquid acid detonates with great violence, even so low as 68°. It is decomposed, often with detonation, by phosphorus, sulphur, and hydrochloric acid.

132. HYPOCHLOROUS ACID is a liquid having the red colour of arterial blood, a strong and penetrating odour resembling at once that of chlorine and that of iodine. It boils at 68°, producing a reddish yellow vapour, having SG=2·977, of which water dissolves about 200 times its volume, or about three-fourths of its weight. This solution has a dark yellow colour, renders the skin yellow and disorganises it, and destroys colours.

Hitherto it has not been applied to any use in its free state; but the salts it forms, combined with bases, are extensively used as bleaching agents.

133. THE COMPOUND OF CHLORINE AND HYDROGEN, presents the first example of the class of hydracids. Its composition is HCl, and it is called Hydrochloric acid.*

* Formerly called *muriatic acid*, a name which ceased to be applicable when Davy, Gay Lussac, and Thenard showed how it ought to be regarded.

134. HYDRACIDS. As already stated it was formerly supposed that oxygen was the only acidifying principle, and from this supposition it derived its name. The discovery of the true nature of chlorine, and the true composition of hydrochloric acid, proved that the presence of oxygen was not necessary to constitute an acid. But whether the acidity of the compound HCl, was due to the hydrogen or to the chlorine, remained to be ascertained.

The discovery of analogous compounds of hydrogen with iodine, bromine, and fluorine, all possessing strong acidity, left no doubt that the acidifying constituent was hydrogen.

A class of binary compounds consisting of combinations of a single equivalent of hydrogen, with single equivalents of chlorine, iodine, bromine, and fluorine, were therefore distinguished from the acids supposed to derive their characteristic property, from oxygen, by the name of hydracids, and were severally denominated—

Hydrochloric acid . . .	HCl	Hydrobromic acid . .	HBr
Hydriodic acid . . .	HI	Hydrofluoric acid . . .	HF

All these compounds have a close mutual analogy. Each is formed of equal volumes of hydrogen and the other constituent, which is called the *radical* of the acid, and in each case they combine without either condensation or expansion, and since the equivalent by volumes of hydrogen is 1, that of these hydracids is 2.

But these are not the only cases in which hydrogen plays the part of an acidifier. It combines equivalent for equivalent, with sulphur, selenium and tellurium to form—

Hydrosulphuric acid	HS
Hydroselenic acid	HSe
Hydrotelluric acid	HTe

In the case of these acids the equivalents by volume are 2.

Of these hydracids, hydrochloric, hydrofluoric, and hydrosulphuric alone possess sufficient importance to be further noticed.

135. HYDROCHLORIC ACID is a colourless gas, of irritating odour, which diffuses white fumes in humid air. Its SG = 1·2474. When respired it excites coughing. Under a pressure of 40 atmospheres, and at a temperature of 50° it is reduced to a colourless liquid of SG = 1·27. It is incombustible and very soluble in water, which at 32° dissolves 480 volumes of the gas. So strong is the affinity of this gas for water, that if a test-glass filled with it be inverted over water, that liquid will rush up the glass with such force as sometimes to produce its fracture.

A saturated solution of the gas at 32° has SG = 1·2109, and contains 6 equivalents of water. It is therefore HCl, 6HO. When exposed to the air a part of the acid evaporates, and it is reduced to HCl, 12HO, with SG = 1·128, at 57°.

A solution submitted to distillation liberates at first a great quantity of gas, but its boiling point soon becomes fixed at 230°, when its SG = 1·094, and its composition is HCl, 16HO. There are therefore three hydrates of this acid containing respectively 6, 12, and 16 equivalents of water.

Hydrochloric acid blackens and soon destroys organic com-

pounds. In general it is without effect upon the metalloids. Several metals, such as potassium, iron, and tin, decompose it, combining with the chlorine and liberating the hydrogen. The great facility with which it is decomposed in the cold, by iron and zinc, causes it to be sometimes employed in the preparation of hydrogen. At a high temperature it is decomposed by silver. It reacts upon the metallic oxides, producing water and the chlorides, thus :—

$$HCl + MO = MCl + HO.$$

136. PREPARATION. By decomposing chloride of sodium, NaCl, common salt, by means of hydrated sulphuric acid, SO_3, HO, thus—

$$NaCl + SO_3, HO = \underbrace{NaO, SO_3}_{\text{Sulphaté of soda.}} + HCl.$$

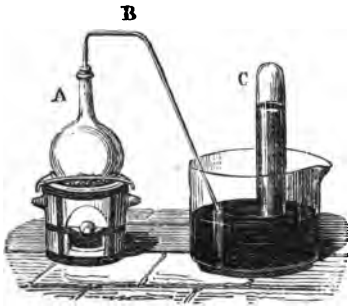


Fig. 104.

The process is conducted in an apparatus such as that shown in *fig.* 104. The salt is placed in the mattras A, and upon it the sulphuric acid is poured. On slightly heating the mattras the gas will pass off by the transfer tube B, and should be collected over mercury in C, as it would be absorbed by water.

137. USES. As a test to determine the presence of the salts of silver, the protoxides of mercury, lead, to decompose the carbonates and sulphurets, to detect ammonia, and determine its quantity, &c. In the arts and manufactures it is used for the preparation of chlorine, of the bleaching chlorides, for the extraction of gelatine from bones, and various other purposes. Alone or mixed with nitric acid, forming *aqua regia*, it is used to dissolve a great number of metals and alloys, and in the preparation of metallic chorides.

138. AQUA REGIA is a mixture of hydrochloric and nitric acids, in the proportion of one measure of the former to two or three of the latter. This mixture is used to dissolve gold and other metals, which neither of the component acids separately will attack.

BROMINE.

139. BROMINE is a reddish brown liquid, highly poisonous, of a disagreeable taste, strong and penetrating odour, from which it takes its name, βρῶμος (bromos), fetidness. It gives a yellow colour to organic compounds, and destroys them. Its SG=2·966. It congeals at 7·6°, and is easily volatilised. It boils at 145·5°, and its vapour has SG=5·3933. It is sparingly soluble in water, but sufficiently so in alcohol. It is soluble in all proportions in ether. It forms with water a hydrate which is solid and crystallisable. Like chlorine it has a strong affinity for hydrogen, and destroys colours. Being less ener-

getic than chlorine it is displaced by the latter from its compounds. It readily combines with a great number of the metals.

It is of little use in chemistry, but has been employed of late in photography.

Bromine is found combined with potassium, sodium, or magnesium, in sea water, and in the liquid of many salt springs. Bulhier has found it united with silver, forming the native bromide of that metal.

IODINE.

140. IODINE is a solid having the odour of chlorine and bromine, and a metallic grey colour resembling plumbago. At 62·5° its SG=4·948. It fuses at 225°, and boils at 356°. In volatilising it forms a violet vapour, from which it takes its name ἰώδης (iodes) violet, having SG=8·716. It is almost insoluble in water, but is very soluble in alcohol, to which it imparts a dark brown colour. Crystals of iodine are deposited from such a solution by evaporation.

141. Iodine destroys organic compounds, and stains the skin and paper yellow. In its other reactions it resembles chlorine and bromine, but its affinities are more feeble.

In contact with starch, it produces a blue compound called the iodide of starch. This loses its colour when raised to 160° or 170°, but recovers it on cooling. By this property of rendering starch blue, the presence of the smallest quantity of iodine can be detected.

USES. Both in its free state and combined with potassium, it is used in medicine for the cure of goître and scrofulous maladies. It is also used in photography.

It is found in nature combined with sodium in marine plants, in sponge, in sea water, and in the water of salt springs, and in the mineral kingdom in combination with silver, as the native iodide of that metal.

FLUORINE.

142. FLUORINE has never been obtained in the uncombined state. Its existence is only inferred from its compounds, which have a close analogy with those of chlorine, iodine, and bromine. It is found native in combination with calcium, the compound being *fluor spar*. In the animal organism it enters in a minute proportion into the composition of the bones, teeth, and is occasionally found in urine.

The difficulty of obtaining it in a separate state arises from its strong affinities, which cause it when separated from one body to enter immediately into combination with another, derived from the material of the apparatus in which the experiment is made. It has been conjectured, from some experiments of Knox and Baudrimont, that it is a coloured gas resembling chlorine.

143. HYDROFLUORIC ACID, HF, the most important of its compounds, is obtained by the action of sulphuric acid SO_3, HO on fluor spar CaF.

$$SO_3,HO + CaF = \overbrace{CaO,SO_3}^{\text{Sulphate of lime.}} + HF.$$

The pulverised fluor spar mixed with the acid is gently heated in a retort, such as that represented in *fig.* 105, and the acid is condensed in the U-shaped receiver, which for that purpose is immersed in a freezing mixture, C, *fig.* 106.

This acid is liquid, diffuses thick fumes in air, has SG = 1·06 and boils at 68°. A drop let fall on water dissolves with a noise like the hissing of red hot iron immersed in that liquid. When concentrated, it is one of the most corrosive substances known.

The metalloids in general have no action upon it. With the exception of gold, platinum, and lead, all the metals decompose it, combining with the fluorine and disengaging the hydrogen.

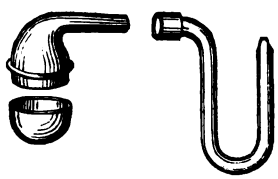


Fig. 105.

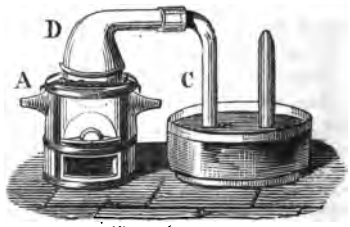


Fig. 106.

144. The most remarkable reaction of this acid is effected upon silex, SiO_3, which produces water and a gaseous compound called FLUORIDE OF SILICON.

$$\underbrace{SiO_3}_{\text{Silex.}} + \overbrace{3HF}^{\text{Hydrofluoric acid.}} = \overbrace{SiF_3}^{\text{Fluoride of silicon.}} + 3HO.$$

Upon this reaction depends the application of hydrofluoric acid to etching on glass. The plate to be etched is first covered with a thin coat of wax. The design intended to be engraved is then drawn upon the plate by proper instruments, by which the coating of wax is removed from all parts intended to be traced. A dilute solution of hydrofluoric acid being then poured upon the plate, corrodes all the parts of the glass from which the wax has been removed, by acting upon the silex which is a constituent of the glass, and thus the design is engraved.

CHAPTER VIII.

SULPHUR.—PHOSPHORUS.

SULPHUR.

145. SULPHUR is a solid of a peculiar light yellow colour, without taste or odour, but developing when rubbed a characteristic odour ; a bad conductor of heat and electricity, insoluble in water, and almost so in alcohol and ether. It is very friable, splitting to pieces with a crackling noise by the warmth of the hand owing to its unequal expansion. Its SG = 2·087. It melts at 230°, and boils at 860°. It may be easily separated from impurities by distillation, being sufficiently volatile. Its vapour has SG = 6·617.

Between its points of fusion and volatilisation it undergoes some remarkable changes. When fused, it is converted into a yellow liquid having perfect

fluidity, which, on being cooled, becomes solid sulphur of a yellow colour, such as it was before fusion. But if, after fusion, its temperature be gradually raised from 230° to 290° or 300°, its colour becomes darker, and at 370° to 380° it becomes orange, its fluidity being destroyed and its consistency being rendered viscous. At 390° it becomes brown, and it is so viscid that the vessel which contains it can be inverted without causing the sulphur to flow out. By a continued elevation of temperature the sulphur recovers its fluidity. If, in this state it be cooled by pouring it into cold water, it will become pasty, transparent, will preserve its brown colour, and will acquire the elasticity of caoutchouc, so that it may be drawn out into long threads. It is only after a long interval that it can resume its proper yellow colour and natural solidity.

146. Sulphur is crystallisable and dimorphous, that is, it is capable of crystallising under different conditions in two incompatible forms. If it be crystallised by evaporation from a solvent, such as the sulphuret of carbon, its crystals are elongated octohedrons of the fourth system. If it be crystallised by fusion and cooling, it will assume the form of long prismatic needles of the fifth system. If these be left for some time undisturbed, they will gradually lose their transparency, and be changed into elongated octohedrons of the fourth system, differing from crystals of native sulphur only by their opacity, §§ 56, 57.

147. Sulphur is universally diffused in nature. It occurs in abundance native in all volcanic districts. It constitutes an important article of commerce in Sicily. In combination with oxygen it is found in innumerable natural substances, as gypsum or plaster of Paris, and the native sulphates of numerous metals. Combined with hydrogen it constitutes part of a large class of mineral waters. It is also found in certain animal substances, essential oils, and so on.

148. Uses. It is extensively employed in the industrial arts. It is applied to the formation of moulds and for taking impressions. Mixed with carbon and saltpetre it forms gunpowder. Transformed by combustion into sulphurous acid it is used for bleaching wool and silk. It is also used in the manufacture of vitriol, and in the fabrication of matches; in medicine, it is applied in the treatment of cutaneous diseases, and holds an important place in general among therapeutic agents.

149. The compounds of sulphur and oxygen are numerous, but the most important are sulphurous and sulphuric acids. There are however, four others, which form a series of acids called *thionic* (from, *θεῖον* theion, sulphur), the composition of which is S_2O_5, S_3O_5, S_4O_5, and S_5O_5. It will be sufficient here to notice the two first.

150. Sulphurous acid, SO_2, is a colourless, irrespirable, incombustible gas, of an acid disagreeable taste and irritating characteristic odour, being that produced by burning a sulphur match. If respired it acts upon the lungs producing convulsive coughing. It first reddens, and then bleaches litmus. Its SG = 2·234. It is liquified at the temperature of 5°, and solidified by the combination of cold and pressure.

Water dissolves about fifty times its volume of sulphurous gas at 68° and under the common pressure of the air. The solution thus obtained has all the properties of the pure gas. It acts as a strong acid, dissolving several metals.

It bleaches most organic coloured substances without destroying them. It is used therefore in bleaching wool and silk, to which chlorine would give a yellowish colour.

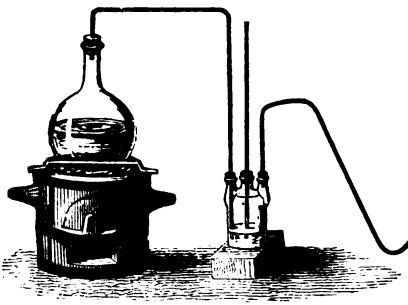


Fig. 107.

151. PREPARATION. Let 6 parts of the peroxide of manganese MnO_2, pulverised, be well mixed with 1 part of the flowers of sulphur, and placed in a glass retort over a charcoal fire. The manganese will give up one equivalent of its oxygen to the sulphur, converting it into sulphurous acid, which will pass off as gas while the protoxide of manganese remains.

$$2MnO_2 + S = 2MnO + SO_2.$$

The apparatus is shown in *fig.* 107. The gas coming over is transmitted through a washer, which retains any small portion of sulphur which is volatilised.

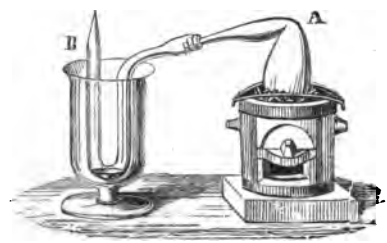


Fig. 108.

152. THE LIQUID ACID is prepared by the reaction of copper on concentrated sulphuric acid, in a glass retort, *fig.* 108, connected with a U-shaped condenser, immersed in a mixture of pounded ice and common salt, in which the gas is reduced to the liquid state.

The liquid acid is colourless, very fluid and volatile, it boils at 14°. Its SG = 1·45. In evaporating suddenly it produces a cold sufficiently intense to congeal mercury, and to liquify certain gases; chlorine and ammonia for example. Evaporated in vacuo, it produces a cold of −90°. In this case it is partly solidified. It is congealed by exposure to a mixture of ether and solid carbonic acid.

153. SULPHURIC ACID, one of the most important chemical products, is presented in several states :—

1. Anhydrous . . .	SO_3	4. Third hydrate . .	$SO_3,3HO$
2. Monohydrated . .	SO_3,HO	5. Nordhausen . .	$2SO_3,HO$
3. Second hydrate . .	$SO_3,2HO$		

154. ANHYDROUS SULPHURIC ACID, SO_3, is a solid consisting of white silky tufts like amianthus. It may be compressed between the fingers without affecting them. Its SG = 1·97. It fuses at 68°, and volatilises at 86°.

Its vapour has SG = 2·763. It dissolves sulphur, producing compounds which are brown, green, or blue, according to the

proportion of sulphur they contain. At a red heat it is resolved into sulphurous acid and oxygen. It diffuses thick white vapours in the air, and strongly attracts moisture. Its centesimal composition is sulphur 40, and oxygen 60.

This dry acid is usually prepared by distilling the acid of Nordhausen, $2SO_3$, HO, in an apparatus such as that shown in *fig.* 108.

The acid properties of this compound are only developed when it is in contact with water, from which many chemical authorities infer that they do not properly belong to it, but are due to the reaction of the hydrogen of the water upon it, § 135.

155. NORDHAUSEN ACID, the strongest liquid sulphuric acid, may be regarded as a solution of anhydrous in monohydrated acid.

$$SO_3 + SO_3,HO = SO_3,2HO.$$

This acid is a liquid usually brown, a colour however not proper to it, but due probably to organic substances, carbonised by the sulphuric acid. It is a fuming liquid which may be crystallised by cold. It has the property of dissolving indigo more freely than common sulphuric acid, and is on that account used by preference in blue dyeing. It has the further advantage over sulphuric acid, that it never contains nitric acid, which rapidly converts indigo into a yellow substance.

156. HYDRATED OR COMMON SULPHURIC ACID is a colourless inodorous liquid, which at 68° has SG = 1·842. From its oleaginous consistency it is commonly called *Oil of Vitriol.* Its avidity for water causes it to destroy a great number of organic compounds. It boils at 617°. At common temperatures, it exhales no vapour of sensible tension. When concentrated it is congealed at −31°.

It is one of the strongest acids. Even when diluted with 1000 times its volume of water, it reddens litmus. Under the influence of heat, it expels most other acids from their combinations.

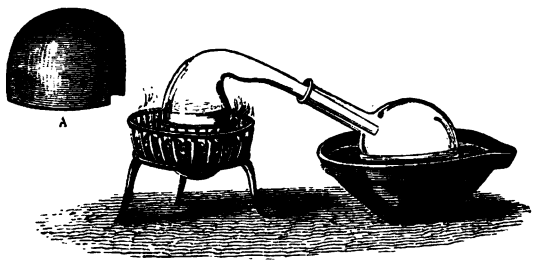


Fig. 109.

When diluted it is concentrated by distillation. This process is conducted in a common retort and condenser, but with some precautions. Since the violent ebullition of so heavy a liquid might break the retort, the grate is so contrived that the fire is applied only to the superior stratum of the liquid, *fig.* 109, and a

sheet-iron cap, A, is provided to cover the retort, so as to diffuse and equalise the heat, and prevent condensation at the top of the retort.

The vapour of sulphuric acid is decomposed by a red heat, being resolved into sulphurous acid, water, and oxygen.

$$SO_3,HO = SO_2, + HO + O.$$

157. The metalloids have but little action on it. Carbon takes a part of its oxygen, reducing it to sulphurous acid, and sulphur, by the action of heat, reduces it to sulphurous acid and water.

158. It attacks a great number of metals. The effect of the dilute acid on zinc has been already explained, § 87. Other metals such as lead, copper, mercury, and silver, decompose it, under the influence of heat, and transform part of it into sulphurous acid, forming sulphates with the undecomposed acid.

$$\underbrace{Cu}_{\text{Copper.}} + 2(SO_3,HO) = \overbrace{CuO,SO_3}^{\text{Sulphate of copper.}} + 2HO + SO_2.$$

159. This acid has so strong an affinity for water, that if it be placed in a humid atmosphere, it will absorb altogether its moisture, and render it dry.

This experiment may be performed by placing a capsule of sulphuric acid under a receiver, containing air charged with moisture. The humidity will be immediately absorbed.

160. If a capsule of water be placed with a dish of sulphuric acid under an exhausted receiver, the acid will rapidly absorb the vapour of the water, and thus stimulating the evaporation, will produce such a fall of temperature, that the unevaporated water will be congealed.*

161. Exposed to humid air the acid absorbs 15 times its weight of water. In absorbing water the temperature rises, and may exceed 212°. The heat developed is greatest when 50 parts by weight of the acid has absorbed 15 of water.

162. The acid mixed with snow or pounded ice, produces heat or cold, according to the proportions mixed. The combination developes heat, but the melting of the snow absorbs it. If the former develope more than the latter absorbs, there will be an elevation of temperature; but if the absorption exceed the development, there will be a fall. Thus while 4 parts of acid, with 1 part of snow, produce heat, 4 parts of snow, with 1 of acid, produce cold.

163. If a mixture of the acid and water be allowed to descend to its original temperature, the volume will be found to be less than the sum of the volumes mixed. The greatest amount of this contraction is 3 per cent of the original sum of the volumes. In this case hydrates are produced, the composition of which is $SO_3, 2HO$ or $SO_3, 3HO$. These have but little stability, and are soon reduced by evaporation to SO_3, HO.

164. Uses. This acid is employed in numerous arts and manufactures, and indeed in nearly all which involve chemical processes. It is most largely employed

* See Handbook of Nat. Phil., Heat (529).

in the fabrication of soda, from the sulphate of that alkali. Also in the preparation of alum, of sulphate of iron, chlorine, phosphorus, glucose or grape sugar, sulphuric ether, and ethers in general, stearine candles, in the purification of oil, and various other processes.

It is of all others, the reagent most frequently employed in the laboratory.

165. THE COMPOUNDS OF SULPHUR AND HYDROGEN are two :—

1. Hydrosulphuric acid . . . . . HS.
2. The bisulphuret of hydrogen . . . . . HS_2.

It will be sufficient here to notice the former.

166. HYDROSULPHURIC ACID, more commonly called *sulphuretted hydrogen*, is a colourless gas whose fetid odour, resembling that of rotten eggs, is one of its most characteristic properties. Its SG = 1·1912. It affects litmus like the weaker acids, giving it a wine-red colour. At common temperatures, under a pressure of 17 atmospheres, it becomes a colourless liquid of great fluidity, with SG = 0·90, and with strong refractive power. An atmosphere containing a 1500th of its volume of this gas, immediately killed a linnet, an 800th killed a dog of average size, and a 200th killed a horse.

It is inflammable, burning with a blue flame, the products of combustion being sulphurous acid and water—

$$HS + 3O = HO + SO_2.$$

Water dissolves about three times its volume, at 50°, and alcohol dissolves 6 times its volume of the gas.

Chlorine decomposes it, producing hydrochloric acid and sulphur,

$$Cl + HS = HCl + S.$$

167. PREPARATION. By decomposing a metallic sulphuret by an acid.

$$\overbrace{FeS}^{\text{Sulphuret of iron.}} + SO_3,HO = \overbrace{FeO,SO_3}^{\text{Sulphate of iron.}} + HS.$$

This acid may be decomposed by heating it with any metal which will combine with its sulphur, separating the hydrogen. Tin serves for this purpose. Let a known volume of the gas be introduced into a bent tube, *a b c*, *fig.* 109 A, closed at *c*, and with it a bit of tinfoil. On heating the tube with a spirit lamp, the tin will combine with the sulphur, producing the sulphuret of that metal, and the hydrogen will be separated. The increase of weight of the tin will give the proportion of sulphur in the given volume of the gas.

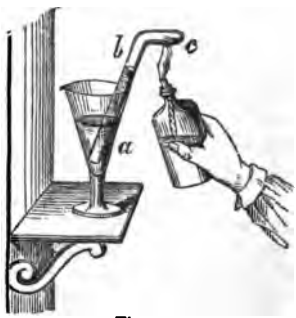


Fig. 109 A.

168. USES. It is one of the reagents most frequently employed in analysis. Sulphureous waters impregnated with this gas, are used as baths for cutaneous maladies.

PHOSPHORUS.

169. PHOSPHORUS is a pale yellowish, or rather colourless solid, without taste or smell. Its vapour however has an alliaceous odour, and in solution it has an acid disagreeable savour. It is translucent, and has a waxy consistency, being elastic, and soft enough to be marked with the nail. Its point of fusion is 112°, and of boiling 554°. Its SG=1·83, and that of its vapour is 4·355. It is insoluble in water, but soluble in alcohol, ether, the oils, sulphuret of carbon, and chloride of phosphorus. It does not crystallise by fusion, but rhomboidal dodecahedral crystals of the regular system are deposited from its solutions in any essential oil, or the sulphuret of carbon or phosphorus. Its best solvent is sulphuret of carbon.

170. Phosphorus, by the application of heat, undergoes several remarkable molecular changes. When fused and slowly cooled it remains liquid at temperatures much below its point of fusion; but, like water in the like case, it suddenly solidifies if touched by any other body, and the temperature suddenly rises. If it be exposed to a temperature of 158° and suddenly cooled, it becomes black. By exposure to direct solar light in vacuo, or in a gas which has no action upon it, it becomes red.

171. This *red phosphorus*, also called *amorphous*, is much less fusible than common phosphorus, its point of fusion being 482°, while that of common phosphorus is 112°. If it be raised to 500°, it returns to the state of common phosphorus. If it be kept at a temperature a little lower than 500°, it is converted into a hard compact, violet brownish mass, much less alterable than red phosphorus.

If ordinary phosphorus be kept for some time in water, it loses its transparency, and becomes yellow and opaque, and is invested with a thick yellowish coating.

172. Phosphorus takes its name from its property of being luminous in the dark (φῶς (phos), light; and φέρω (phero), I bear). Characters traced upon a wall or table with a stick of phosphorus, are luminous in a dark place, and are said to be *phosphorescent*. This light proceeds from the slow combustion of the particles of phosphorus.

Phosphorus is highly combustible, and requires when manipulated to be kept under water, as the warmth of the hand is often sufficient to inflame it, and in such cases it inflicts burns which produce frightful injuries, owing to the phosphoric acid, a highly corrosive compound, which is the product of the combustion, and which remains in the wound.

When burnt in air it produces a vivid light, but one still more intense when burnt in oxygen.

173. Phosphorus combines in 3 proportions with oxygen, and unites directly with chlorine, bromine, iodine, and sulphur.

In combination, as phosphate of lime, and magnesia, this element is found abundantly in the bones of animals, from which a supply is exclusively derived by chemical processes. It is also present in animal and vegetable fibrine, and albumen, in urine, and the excrements. In the mineral kingdom it occurs as the phosphates of lime, alumina, lead, copper, &c.

174. USES. This element, the commerce in which has of late immensely increased, is chiefly employed in the fabrication of lucifer matches, and in the laboratory for the analysis of air, § 99, and the preparation of phosphoric acid, and other phosphorus compounds.

175. THE COMBINATIONS OF PHOSPHORUS WTH OXYGEN are four, three of which are acid, and the fourth an indifferent oxide.

1. Phosphoric acid . . . . . PO_5
2. Phosphorous acid . . . . . PO_3
3. Hypophosphorous acid . . . . . PO
4. Oxide of phosphorus . . . . . P_3O_2

176. ANHYDROUS PHOSPHORIC ACID is a white solid, usually formed in very deliquescent filamentous flakes. Immersed in water it is hydrated with a hissing noise, like that of red hot iron. It is volatilised at a white heat without decomposition. Its point of volatilisation being so elevated, it is capable of displacing sulphuric acid from its combinations. It is decomposed by carbon, under the influence of heat, producing carbonic acid, carbonic oxide, and phosphorus.

$$PO_5 + 4C = CO_2 + 3CO + P.$$

Its affinity for water is so great, that when heated with hydrated sulphuric acid it dehydrates it.

$$PO_5 + SO_3,HO = PO_5,HO + SO_3.$$

In virtue of this affinity it is often employed for drying gases. It also serves in chemical researches for dehydrating certain organic compounds. It sometimes determines the combination of the oxygen and hydrogen of such bodies, absorbing the water thus produced.

177. PREPARATION. It may be obtained conveniently by means of the apparatus shown in *fig.* 110. Air well dried by passing through *cc*, which contains pumice saturated with oil of vitriol, is drawn through the globe A, in which phosphorus is burnt in a capsule *v*, the product of combustion, the anhydrous acid, being collected in B.

178. THE HYDRATES OF PHOSPHORIC ACID are three, which contain severally 1, 2, and 3 equivalents of water. These compounds differ from the hydrates of most other acids, in as much as they are wholly different one from another in their properties. They are denominated—

1. Monohydrated, or metaphosphoric acid . . PO_5,HO
2. Bihydrated, or pyrophosphoric acid . . $PO_5,2HO$
3. Trihydrated, or common phosphoric acid . . $PO_5,3HO$

These three hydrates form with bases three distinct series of salts, in which in all cases the metal takes the place of the hydrogen, so that the first series contains, 1 equivalent of the base, the second 2, and the third 3. The composition of the three series of salts is accordingly—

$$MO,PO_5\ ;\ 2MO,PO_5\ ;\ 3MO,PO^5.$$

179. According to the new system indicated in § 41, *note*, the forms of these compounds would be expressed thus—

Acids	$H,PO_6,2H,PO_7,3H,PO_8$.
Salts	$M,PO_6,2M,PO_7,3M,PO_8$.

In this case, PO_6, PO_7, and PO_8, are regarded as compound radicals, playing the same part in the acid and salt, as chlorine plays in hydrochloric acid and common salt.

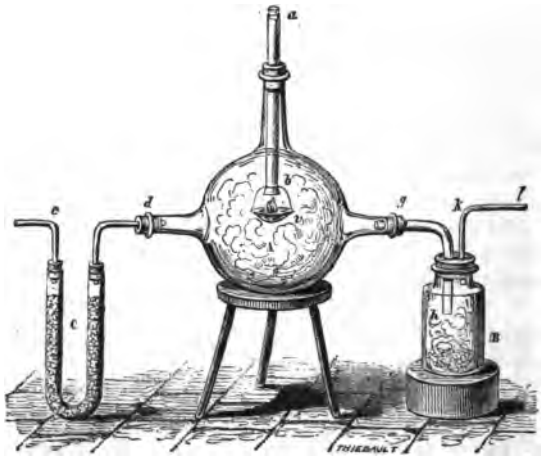


Fig. 110.

The three hydrates are also denominated from these properties, *monobasic*, *bibasic*, and *tribasic*.

180. The bases of the phosphates $3MO,\ PO_5$ may be partially replaced by corresponding equivalents of water, which in these cases appears to play the part of a base. Thus we have—

Phosphates.	Pyrophosphates.
$3MO,PO_5$	$2MO,\ PO_5$
$2MO,HO,PO_5$	$MO,\ HO,\ PO_5$.
$MO,2HO,PO_5$	

The term, *neutral salts*, was formerly restricted to salts consisting of single equivalents of the acid and base. Since, however, a neutral phosphate contains 3, and a pyrophosphate 2 equivalents of the base, the signification of the term must be extended.

181. METAPHOSPHORIC ACID, $PO_5,\ HO$, is a vitreous, uncrystallisable solid. If an aqueous solution of the anhydrous acid be heated in a platinum capsule, until it loses by evaporation all the water which it will part with, a mass will remain, which will fuse at a red heat, to a transparent semifluid substance,

which solidifies in the form of a vitreous mass. This is metaphosphoric acid. It appears, therefore, that the single equivalent of water which it contains cannot be separated from it by heat alone.

Metaphosphoric acid in contact with water is successively converted into pyrophosphoric and common phosphoric acid. It coagulates albumen, and forms with the soluble salts of baryta a white precipitate. It precipitates the salts of lime and silver in the form of white glutinous masses.

182. PYROPHOSPHORIC ACID, PO_5, 2HO, like the former, is vitreous, but it crystallises, retaining its 2 equivalents of water. It precipitates neither albumen nor the salts of baryta. Saturated by a base, like soda and potash, it forms salts, which give a white precipitate with solution of silver.

183. COMMON PHOSPHORIC ACID, PO_5, 3HO, is inodorous, with a strong acid taste, reddens litmus, and, when heated, is fused into a vitreous mass. By calcination it is converted successively into pyro- and metaphosphoric acid. It is volatilised at a high temperature. It attacks glass and porcelain. It is reduced by carbon.

It is characterised by the yellow insoluble salt which it forms with the protoxide of silver.

184. PHOSPHOROUS ACID, PO_3, when hydrated, is PO_3, 3HO. When it combines with bases to form phosphates, it parts with 2 equivalents of water. The hydrated acid crystallises in transparent parallelopipeds, and is resolved by heat into phosphoric acid and phosphuretted hydrogen. It has a strong affinity for oxygen, and can reduce some metallic oxides. It also decomposes the salts of gold and silver.

185. HYPOPHOSPHOROUS ACID, PO, is not known anhydrous. Its hydrate is PO, 3HO. This loses 1 equivalent of water when it combines with bases to form hypophosphites, the composition of which is MO, PO, 2HO. This acid is white and viscous, having a strong affinity for oxygen. It is resolved by heat into phosphoric acid and phosphuretted hydrogen, mixed with the vapour of liquid phosphuretted hydrogen, which renders it inflammable. It reduces certain metallic oxides, as, for example, that of lead, being transformed into phosphoric acid. It may be distinguished from phosphorous acid by depositing sulphur when heated with sulphuric acid. It decomposes sulphate of copper by ebullition, depositing the metal and disengaging hydrogen.

186. OXIDE OF PHOSPHORUS, P_2O, is found in two isomeric states, the *red* and the *yellow*.

187. *The red oxide* has the colour of red lead (minium), is without odour, is heavier than water, does not shine in darkness, resists the temperature of boiling mercury, and is transformed at a red heat into phosphoric acid and phosphorus:—

$$5P_2O = PO_5 + 9P.$$

It inflames in contact with nitric acid, and detonates when mixed with chlorate of potash. It is insoluble in water, alcohol, ether, and the essential oils.

It is prepared by burning phosphorus in air or under water.

188. *The yellow oxide* is soluble in potash. At 300° it is transformed into the red oxide. It combines with potash and ammonia, forming brown compounds.

It is prepared by dissolving phosphorus in its own protochloride, and leaving the liquor exposed to air and light.

189. THE COMPOUNDS OF PHOSPHORUS AND HYDROGEN are three, liquid, solid, and gaseous:—

1. Liquid phosphuret . . . . . PH_2.
2. Solid phosphuret . . . . . P_2H.
3. Gaseous phosphuret . . . . . PH_3.

190. THE LIQUID PHOSPHURET, PH_2, is colourless, is not congealed at a temperature of 4°, and is decomposed at 86°. It is insoluble in water, is decomposed by the essence of turpentine, and has a high refracting power. It is highly inflammable, burning spontaneously with a brilliant flame when put in contact with air. Under the influence of light it is decomposed :—

$$5PH_2 = P_2H + 3PH_3.$$

Mixed in the smallest proportion with any inflammable gas, it will render it spontaneously inflammable.

191. It is prepared by decomposing the phosphuret of calcium by water, and collecting the liquid in a cold receiver, mixed with the gas which is disengaged.

192. THE SOLID PHOSPHURET, P_2H, has a fine yellow colour, and exhales a faint odour of phosphorus. It reddens by exposure to light, is not luminous in the dark, and does not inflame until raised to 350°. Heated to 380°, out of contact with oxygen, it resists decomposition ; but, at a somewhat higher temperature, is resolved into hydrogen and the vapour of phosphorus. It is insoluble in water and alcohol ; but when left in water, exposed to direct solar light, it is gradually dissolved, disengaging hydrogen, and being transformed into phosphoric acid. It detonates when mixed with chlorate of potash, oxide of copper, or oxide of silver.

193. It is prepared by leaving over water test-glasses which contain phosphuretted hydrogen.

194. GASEOUS PHOSPHURET, PH_3, generally known as phosphuretted hydrogen, is a colourless gas, with a characteristic alliaceous and very fetid odour. Its SG = 1·185. Water dissolves only the eighth part of its volume, but it is much more soluble in alcohol, ether, and the essence of turpentine.

It is very combustible. When mixed with the vapour of the liquid phosphuret it inflames spontaneously in air; and each bubble, as it rises from the surface of the mercury or water under which the gas is evolved, burns with a slight explosion, producing a current of smoke, which enlarges gradually and regularly as it rises, *fig.* 111.

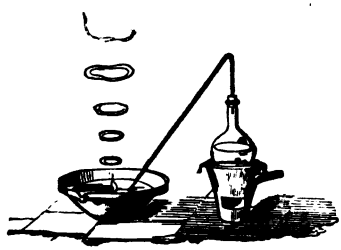


Fig. 111.

Chlorine decomposes this gas with a disengagement of heat and light. Several metallic chlorides, those of tin and antimony, for example, combine with it. Water decomposes these compounds, disengaging a gas which does not inflame in air.

195. This gas is obtained pure by decomposing the phosphuret of calcium by liquid hydrochloric acid.

196. THE CHLORIDES of phosphorus are two, the protochloride PCl_3, and perchloride PCl_5.

197. THE PROTOCHLORIDE, PCl_3, called also the terchloride, is a colourless liquid, which fumes in air, and boils at 172·4°. Its SG = 1·45, and that of its vapour 4·742. Water decomposes it, transforming it into hydrochloric and phosphorous acids.

$$PCl_3 + 3HO = PO_3 + 3HCl.$$

The preparation of phosphorous acid depends on this reaction.

198. This compound is prepared by transmitting a current of dry chlorine over phosphorus present in excess. The chlorine is produced in the mattras, A, *fig.* 112, is washed and dried in B and the drying-tube, encounters the vapour of phosphorus evolved in D, and after combination is condensed in E.

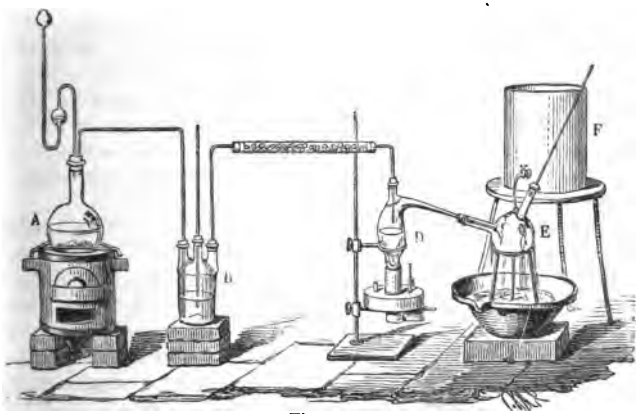


Fig. 112.

199. THE PERCHLORIDE, PCl_5, is a white crystalline solid, which easily melts, and in cooling crystallises in colourless prisms. It boils at 330°. It is decomposed by water, being resolved into phosphoric and hydrochloric acids :—

$$PCl_5 + 5HO = PO_5 + 5HCl.$$

It is prepared by transmitting dry chlorine over the protochloride.

CHAPTER IX.

CARBON.—BORON.—SILICON.

CARBON.

200. CARBON is a solid, without taste or smell, quite infusible at the highest temperatures of the furnaces, and insoluble in all menstrua. In its physical properties, such as colour, transparency, lustre, hardness, density, sonority, and the property of conducting heat and electricity, carbon is subject to variations observable in

no other body to an equal extent. This will be understood when it is stated that substances apparently so different as the diamond, graphite, lamp-black, anthracite, coke, and wood charcoal, are severally carbon, more or less pure.

Carbon, as will presently appear, combines with oxygen, forming two compounds, both gaseous, carbonic oxide and carbonic acid. Meanwhile, it may be stated that one of the most common tests by which the carbon of substances is identified is its power of forming these gases when burned.

201. THE DIAMOND, burned in oxygen, produces pure carbonic acid. It is therefore pure carbon.

It is always distinctly crystallised, often absolutely transparent and colourless, but sometimes having tints of yellow, pink, or blue. Its crystalline form is that of the cube, or one or other of its derivatives. It is infusible and unalterable at the highest temperatures, if air be excluded; but when placed between the poles of a powerful voltaic battery, it is converted into coke or graphite.

It is the hardest known body, but it admits of being readily split in the direction of its planes of cleavage, § 43. It can only be cut or abraded by its own dust, which serves for polishing its facets after being split according to the planes of cleavage. This dust is otherwise very useful to the lapidary and seal engraver.

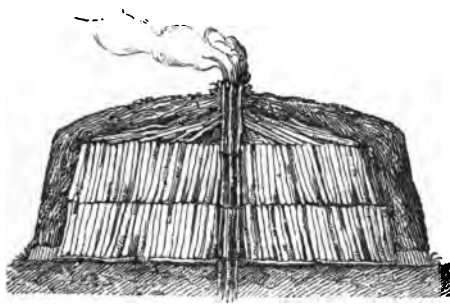


Fig. 113.

A small crystal of diamond set in a convenient socket, with one of its edges presented outwards, is used by the glazier for cutting glass.

Its SG varies from 3·50 to 3·55. It has a high refractive and dispersive power, and is a non-conductor of heat and electricity.

202. GRAPHITE, BLACKLEAD, or plumbago, consists essentially of pure carbon, with accidental traces of iron, varying from 0 to 5 per cent. Its crystals are short six-sided prisms.

203. LAMPBLACK is the soot resulting from the imperfect combustion of certain bodies rich in carbon, such as tallow, oil, and resin. It is carbon in the uncrystallised or amorphous state.

204. ANTHRACITE and WOOD-CHARCOAL are also amorphous carbon. Amorphous carbon differs from crystalline in being a conductor of electricity. Its SG = 2.

205. Charcoal is prepared from wood by the smothered combustion of a pile of faggots covered with earth, *figs.* 113, 114.

206. With free access of air, carbon, when ignited, burns and is completely converted into carbonic acid, with a great evolution of heat. It is to this property that all forms of fuel, of which carbon forms a chief constituent, owe their heating power.

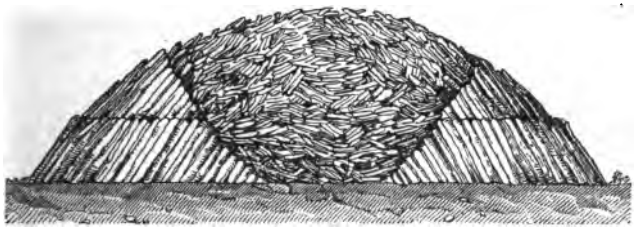


Fig. 114.

207. THE COMPOUNDS OF CARBON AND OXYGEN are principally carbonic oxide, CO, and carbonic acid CO_2. There are, however, several other compounds of subordinate interest :—

Oxalic acid	$C_2\ O_3,\ HO$
Mesoxalic acid	$C_3\ O_4,\ 2HO$
Rhodizonic acid	$C_7\ O_7,\ 3HO$
Croconic acid	$C_5\ O_4,\ HO$
Mellitic acid	$C_4\ O_3,\ HO$

208. CARBONIC OXIDE is a colourless, insipid, inodorous gas, SG = 0·967, completely neutral and scarcely soluble in water. It is combustible, burning with a characteristic blue flame, and producing carbonic acid, $CO + O = CO_2$.

It was long supposed that carbonic oxide was innoxious when respired. Leblanc, however, has shown by experiments on the lower animals, that a proportion of this gas so small as one per cent. is highly deleterious. It would therefore appear that much of the injurious effects ascribed to carbonic acid escaping into rooms from ill-constructed or ill-managed stoves, arises in reality from carbonic oxide evolved in the imperfect combustion of the fuel.

This gas has not been liquified. It is easily dissolved in a solution of the ammoniacal subchloride of copper, Cu_2Cl. It is neutral to litmus, and does not combine either with acids or bases. It is to be regarded, according to Dr. Gregory, as a compound radical, since it acts like an element combining with the elements. It thus combines with chlorine, oxygen, and the metals, and like cyanogen, to be hereafter described, it acts as a compound radical in organic chemistry.

209. PREPARATION. The oxides when heated with carbon give carbonic oxide or carbonic acid, according as they are difficult or easy of reduction. Thus, the

oxide of zinc, ZnO, which is easy of reduction, heated in a stoneware retort A B, *fig.* 115, with carbon, gives carbonic oxide, ZnO+C=CO+Zn.

210. CARBONIC ACID, CO_2, at common temperatures is a colourless gas, with a rather pungent and slightly acid smell, and acidulous taste. Its SG = 1·5290. It renders tincture of litmus dark red, which, however, disappears by exposure to the air or by ebullition.

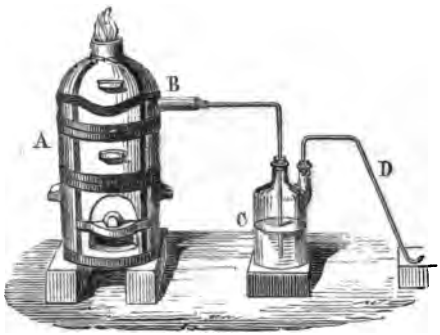


Fig. 115.

It is not altered by the most intense heat, but is decomposed by a series of electric sparks, a phenomenon which is so much the more remarkable, as a mixture of carbonic oxide and oxygen may be made to combine and form carbonic acid by a like series of sparks.

Neither sulphur, nitrogen, chlorine, nor hydrogen have any action on this gas; but at a high temperature it is decomposed by hydrogen and carbon, the former taking from it half of its oxygen to form water, and the latter transforming it into carbonic oxide.

$$CO_2 + H = CO + HO$$
$$CO_2 + C = 2CO$$

It is decomposed by many of the metals. The most oxidable, such as potassium and sodium, take away all its oxygen, and the less so, such as iron, zinc, and manganese, only one equivalent.

$$CO_2 + 2K = C + 2KO$$
$$CO_2 + Zn = CO + ZnO$$

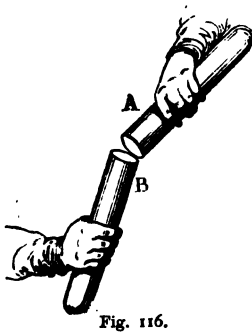


Fig. 116.

The SG being so great, this gas may be poured like a liquid from one receiver to another, *fig.* 116. If produced in any vessel or cavity it will remain at the bottom with the atmospheric air resting upon it. A stratum of this gas is formed at the lower part of the Grotto del Cane at Pozzuoli, near Naples. The depth of the stratum being about two feet, an animal of less height will perish standing in it, while a man may stand there with impunity.

211. This gas is evolved from grape-juice and other liquids in a state of fermentation, so that persons entering a vat, cellar, or other confined space in which such process is in progress, incur the risk of asphyxia.

212. Water under common pressures dissolves its own volume of the gas, but under increased pressure will absorb five or six times that proportion. When the pressure is removed or diminished, the gas escapes from the liquid with effervescence. It is thus that several gaseous beverages, such as soda and selzer waters, are produced.

213. Water charged with carbonic acid parts with the gas when heated, or when placed in a vacuum.

214. The usual test for determining the presence of this gas depends on its property of rendering lime-water turbid. If it be transmitted through lime-water, it will combine with the lime to form carbonate of lime, which being insoluble first renders the water turbid, and then subsides. This precipitate being soluble in carbonic acid itself, care must be taken in such experiments that there be an excess of lime-water.

215. The carbonate of lime, dissolved in a greater or less proportion by the carbonic acid which is found in the water of steam-boilers, is disengaged by heat, and forms a calcareous deposit on the inside surface of the boiler. This deposit, being a non-conductor of heat, intercepts the heat of the furnace, which, accumulating in the metal of the boiler, renders it incandescent, and causes the boiler to burst.

216. PREPARATION. There are various processes adopted in the laboratory, the most common being the decomposition of the carbonate of lime by suphuric acid—

$$CaO,CO_2 + SO_3 = CaO,SO_3 + CO_2.$$

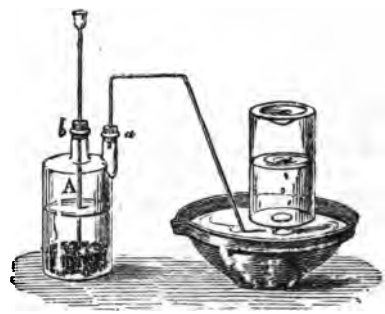


Fig. 117.

Fragments of marble are put in a flask A, *fig.* 117, with a solution of sulphuric acid. The carbonic acid passes over and is collected in a flask.

Hydrochloric may be substituted for sulphuric acid, in which case the reaction is

$$CaO,CO_2 + HCl = CaCl + HO + CO_2.$$

217. This gas is liquified at 32° under a pressure of 36 atmospheres. The liquifaction may be effected by placing a carbonate with sulphuric acid in a strong glass tube closed at both ends, and immersed in a freezing mixture. The gas is then liquified by its own pressure.

218. LIQUID CARBONIC ACID is colourless and soluble in alcohol, ether, and the essential oils. It does not mix with water, and its SG = 0·838 at 32°. It presents the singular phenomenon of a liquid more dilatable than the gases. In passing from the liquid to the gaseous state it produces an extraordinary cold, estimated at 180° below that of melting ice.

219. SOLID CARBONIC ACID is produced by transmitting a current of the liquid acid into a flask or metallic bottle, when a part of it will suddenly pass into the gaseous state, rendering latent a large quantity of heat, which being borrowed from the remainder of the acid, reduces it to the solid state.

The solid acid thus obtained has a temperature 162° below that of melting ice. A still more intense cold is produced by mixing it with ether. Such a mixture will congeal in a few seconds four times its weight of mercury. The mercury thus congealed resembles lead. Medals have been formed of it, which have been preserved for some time in a mixture of ether and the liquid acid.

The effect of solid carbonic acid upon the epidermis is like that of a burn. The fluids of the economy are congealed, the blood coagulated and completely hardened, and a severe inflammation ensues.

Chlorine, nitrous oxide, sulphuretted hydrogen, sulphurous acid and some other gases can be liquified by the cold of a mixture of the solid acid with ether. Cyanogen can be liquified and solidified by it.

220. THE COMPOUNDS OF CARBON WITH HYDROGEN are very numerous. Many of the essential oils, those of roses, lemons, and turpentine, and other organic substances, liquid and solid, such as naphtha, caoutchouc, and napthaline, consist exclusively of carbon and hydrogen. Most of the organic compounds which contain oxygen, when heated with anhydrous phosphoric acid, are deprived of their oxygen, producing compounds of carbon and hydrogen.

All these compounds without exception are of organic origin. There are two, however, both gaseous, which it is convenient to describe in this division of the science. These are protocarburetted and bicarburetted hydrogen.

221. PROTOCARBURETTED, often called *light carburetted hydrogen*, C_2H_4, is a colourless gas, without odour, and insoluble in water. Its SG = 0·556. It burns with a faint bluish flame. It is this gas which issues from stagnant water, and inflaming spontaneously, constitutes the phenomenon commonly called ignis fatuus, Will o' the wisp, Jack o' lantern, and marsh gas. It is easy to verify this, by actually collecting the gas from a stagnant pool, by the arrangement indicated in *fig.* 118.

Fig. 118.

222. This gas produces the *fire-damp* of coal-mines, which in spite of the protection afforded by the safety-lamp, still produces such disastrous accidents. The gas, mixed more or less with bicarburetted hydrogen, issues in abundance from the clefts of the coal seams, and in virtue of its small SG, accumulates in the upper parts of the galleries. Mixed with its own volume of oxygen, it explodes violently, and the same effect ensues if it be mixed with 10 volumes of air, which contain 2 of oxygen. This is the mixture to which the name *fire-damp* is given by the miners. If the proportion of atmospheric air be more than 6 times, and less than 14 times that of the gas, there is always danger of explosion.

223. BICARBURETTED HYDROGEN, or *olefiant gas*, sometimes called *heavy carburetted hydrogen*, C_4H_4, is a colourless gas of empyreumatic odour, SG = 0·9784, which can be liquified by the pressure

of a few atmospheres, or by the cold produced by a mixture of solid carbonic acid and ether. As a liquid it is colourless, and dissolves the resins, oils, and bituminous compounds.

224. This gas is scarcely soluble in water, but is easily dissolved by concentrated sulphuric acid, SO_3, HO. It is in this distinguished from the protocarburet. It is combustible, and burns with a brilliant white flame, having a strong illuminating power. It is decomposed by heat and electricity.

It is prepared by the distillation of alcohol with excess of sulphuric acid.

225. THE CHLORIDES OF CARBON, which are numerous, and of complex composition, all belong properly to organic chemistry.

226. SULPHURET OF CARBON, CS_2, the only compound of carbon with sulphur well-known, is a colourless liquid, with SG = 1·263, having a fluidity equal to that of ether. Its odour is fetid and characteristic, resembling that of sulphuretted hydrogen. It is not sensibly soluble in water, but is soluble in all proportions in alcohol, ether, and the oils. It boils at 113°, the SG of its vapour = 2·67. Being evaporated in a vacuum, it produces a cold of 108° below that of melting ice. Its refracting power exceeds that of all known media. It is highly inflammable, burning with a pale blue flame, and producing by its combustion sulphurous and carbonic acids.

$$CS_2 + 2O = CO_2 + 4SO^2.$$

It readily dissolves sulphur and phosphorus, and these solutions by evaporation give fine crystals of these elements. It also dissolves camphor, the essential oils, and the resins.

PREPARATION. By transmitting the vapour of sulphur over charcoal brought to a red heat in a stoneware or porcelain tube. This process is given in *fig.* 119. Sulphur is introduced from time to time in small fragments at A, the opening being stopped by a cork after its introduction. The tube is slightly inclined towards the condenser E, to facilitate the escape of the sulphuret.

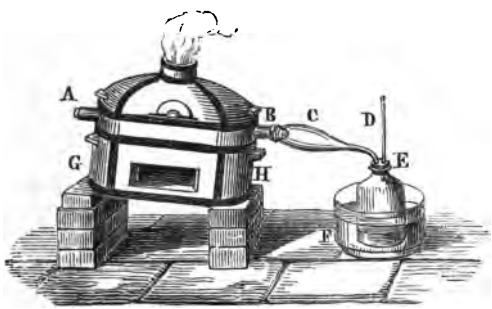


Fig. 119.

USES. It is used as an external application for burns; and in virtue of its solvent power on resins, forms varnishes which dry rapidly, in consequence of the great volatility of the solvent.

227. CYANOGEN, C_2N, is a compound of the highest interest, as being the first example presented of that class of bodies called *compound radicals*, that is, of compounds which enter into combination with the elements and with other compounds, exactly in the same manner as do the elements themselves. It has on this account been found convenient, in the symbolical language of the science, to assign a single symbol to such compounds. Cyanogen is accordingly expressed by Cy, so that $Cy = C_2N$. It combines

with oxygen, producing an oxacid, which may be compared to those of chlorine, bromine, and iodine. Like the metalloids it combines directly with certain metals, producing metallic *cyanides*. So close is the analogy between its compounds, and those of the metalloids, that if its composition had not been so well known, it might very naturally have been classed as one of the elements.

Cyanogen is a colourless gas, of pungent and characteristic odour, having a strong effect on the eyes. Its SG = 1·8064. It is liquified by a pressure of 4 atmospheres, at common temperatures, and produces a colourless liquid, with SG = 0·9. It is solidified by a mixture of solid carbonic acid and ether. Water, dissolves 4, and alcohol 25 volumes of this gas. It is combustible, burning with a purple flame. This property and its pungent smell, are characteristic. Alkaline solutions rapidly absorb it, producing mixtures of *alkaline cyanides* and *cyanates*.

By a small elevation of temperature, it combines directly with potassium and sodium. The other metallic cyanides are produced, generally, by double decomposition, by pouring the cyanide of potassium into a saline solution, containing the metal of which the cyanide is sought.

228. There are various processes by which cyanogen may be obtained in combination. To obtain it in the separate state, the most convenient method is to decompose certain cyanides by heat. The best suited to this purpose is the cyanide of mercury, which was the compound by the study of which Gay Lussac discovered cyanogen. At the temperature of 540° this cyanide is resolved into mercury and cyanogen. In this reaction a small quantity of brown matter is formed, which has exactly the same percentage composition as cyanogen, and has been consequently called *paracyanogen*.

229. HYDROCYANIC ACID, HCy, commonly known as prussic acid, is a colourless liquid with SG = 0·697, at 65°. It is congealed at −22°. It is inflammable, and burns like alcohol, with a yellow flame with bluish tints. It is one of the most acute and subtle poisons. The antidotes are chlorine and ammonia. These remedies however can very rarely be administered in time to neutralise its action on the economy.

PREPARATION. This acid exists in the water distilled from several sorts of stone fruits. It is however produced generally by decomposing a cyanide by an acid. Thus the solution of cyanide of mercury HgCy, treated by hydrosulphuric acid, gives sulphuret of mercury, HgS, and hydrocyanic acid.

$$HgCy + HS = HgS + HCy.$$

The anhydrous acid is prepared by the reaction of hydrochloric acid on the cyanide.

$$HgCy + HCl = HCy + HgCl.$$

The apparatus in which this process is conducted, is shown in *fig.* 120. The cyanide is decomposed in a flask, heated by a small furnace. The tube *a c* contains fragments of marble from *a* to *b*, and pieces of fused chloride of calcium from *b* to *c*, and the U-shaped tube is immersed in a freezing mixture. The

hydrocyanic acid escapes in vapour, mixed with the vapours of hydrochloric acid and water. The hydrochloric being a strong acid, decomposes the marble, CaO,CO_2, in *a b*, and forms the chloride of calcium, water, and carbonic acid.

$$CaO,CO_2 + HCl = CaCl + HO + CO_2.$$

The hydrocyanic, which on the contrary is a very weak acid, has no reaction on the marble. It is a mixture of this latter acid, carbonic acid, and aqueous vapour, which passes through *b c*, where the aqueous vapour is absorbed by the chloride, and the mixture of the other gases passes into the U-tube, where the hydrocyanic acid is condensed, the carbonic acid escaping.

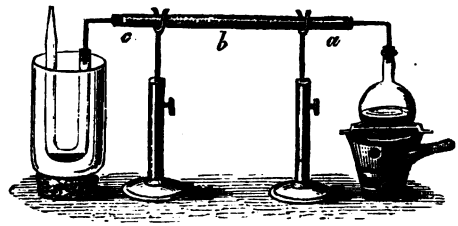


Fig. 120.

Uses. This acid diluted with water is used in medicine, especially in maladies of the chest.

BORON.

230. Boron, like carbon, occurs in 3 forms; the *diamond-like*, the *graphitic*, and the *amorphous*: the last variety is a pulverulent body of a greenish brown colour, heavier than water, without taste or smell, and quite infusible by the strongest furnaces. It has a strong affinity for oxygen, which either free or combined, converts it into boracic acid, BO_3. Mixed with nitre it is oxidised when heated, accompanied often by detonation. It can be fused and volatilised in an atmosphere of nitrogen, by a Bunsen's battery of 600 pairs.

231. Boracic acid, BO_3, which is found native as *borax*, combined with soda, and as *boracite* combined with magnesia, consists of lamellated crystals, without colour or odour, having a very slight taste.

It gives a vinous red colour to tincture of litmus. 100 parts of water dissolve at 68°, 4, and at 212° 34 parts of the acid. Its solution in alcohol burns with a green flame, which characterises it.

It is a weak acid, and can be separated from its compounds by most of the other acids. Nevertheless in consequence of its infusibility, it decomposes the salts of the strongest acids which are more fusible. If for example, it be calcined with sulphate of soda, it will decompose that salt, producing borate of soda, and sulphuric acid, the latter being itself resolved into sulphurous acid and oxygen. It dissolves by fusion the metallic oxides, with which it forms vitreous masses differently coloured according to the metal of the oxide, and these colours seem to characterise the oxide.

The new mode of crystallisation, discovered by Ebelman, and its results, have been already mentioned, § 48.

Boracic acid crystallised, contains 43·6 per cent. of water, its composition being $BO_3,3HO$. At 320° it is changed into a vitreous body, which retains a sixth part of the water contained in the crystallised acid.

232. This acid is found native in small lakes called *Lagoni*, in Tuscany, at the bottom of which small craters, called *suffioni*, constantly disengage the vapour of water, carrying with it boracic acid, *fig.* 121. The acid is dissolved in the water of these *lagoni*, and when the liquor has attained a sufficient degree of concentration, it is only necessary to let it cool to obtain the crystallised acid. The solution of the acid is evaporated by the heat resulting from the condensation of the vapour of the suffioni, which is conducted by flues under the evaporating reservoirs E, F, G, &c.

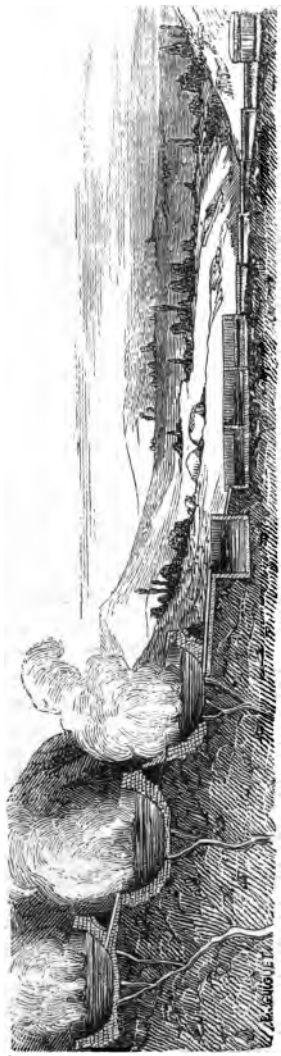


Fig. 121.

233. USES. It is employed in medicine, and in the preparation of borax (borate of soda). It enters into the composition of glass, strass, and the glaze of common earthenware.

SILICON.

234. SILICON (called also *silicium*), like boron and carbon, occurs in 3 forms ; the *diamond-like*, the *graphitic*, and the *amorphous :* the third variety is a yellowish brown pulverulent body without metallic lustre. It is heavier than water. It is a bad conductor of heat and electricity. It cannot be fused by the furnaces, but yields to the heat produced by a powerful voltaic battery. When thus fused and cooled it has sufficient hardness to cut glass, but is less hard than boron similarly treated. When heated in oxygen its combination is slow, being obstructed by the coating of silicic acid which is the first result of the process. When heated with hydrate of potash it is rapidly oxidated, the water of the hydrate being decomposed, the oxygen, combining with the silicon to form silicic acid, which combines with the potash, the hydrogen being disengaged.

Silicon exists naturally only in combination. It is obtained in the separate state by calcining in a glass tube a mixture of potassium and the double fluoride of silicon and potassium. The residuum is treated with water, which dissolves the fluoride of potassium, leaving the silicon insoluble.

Silicon is of all the elements, oxygen excepted, the most universally diffused in nature As silicic acid (silex) it is a principal constituent of all rocks and soils except limestone, rock-salt, and coal. It exists also in solution in certain waters.

235. SILICIC ACID, SiO_3, otherwise called *silica* or *silex*, when anhydrous is a white substance, without taste or smell, infusible in the furnaces, but yielding to the oxyhydrogen blowpipe, by means of which it may be drawn into fine threads. After being raised to a red heat it is completely insoluble in water and the acids, with the exception of hydrofluoric acid, which transforms it into water and the fluoride of silicon.

$$SiO_3 + \underbrace{3HF}_{\text{Hydrofluoric acid.}} = 3HO + \underbrace{SiF_3}_{\text{Fluoride of silicon.}}.$$

This property, which is one of the most striking characteristics of silex, reappears in all the silicates.

236. Hydrogen, carbon, phosphorus, chlorine, and the metals, when present singly, have no reaction upon it. Chlorine and certain metals, particularly iron and platinum, when carbon is present, reduce it, producing carbonic oxide, and a compound of silicon with the reagent. Although it is a very weak acid, it separates the strongest acids from their combinations by heat, in consequence of its high point of fusion.

237. Anhydrous silex is obtained by the calcination of its hydrates.

238. THE HYDRATE, SiO_3,HO, may be obtained by fusing any silicious sand with three or four parts of carbonate of potash, dissolving the fused mass in water, and adding hydrochloric acid by which the hydrate is separated as a jelly.

Ebelman obtained it in hard, transparent masses like rock crystal, by exposing silicic ether to the action of humid air. This hydrate is $2SiO_3,3HO$. Its SG = 1·77.

239. *Opal* is an hydrate of silica, containing from 5 to 13 per cent of water. *Quartz* includes all the native varieties of anhydrous silica, which are characterised by their insolubility in the acids and alkalies. When colourless and crystallised it is called

240. *Rock crystal*. Its SG = 2·65. It is electrified by friction, strikes fire and cuts glass. When a light colour is imparted to it by the peroxide of iron, it is called *false topaz*, and when it receives a violet colour from the presence of the oxide of manganese it is called *amethyst*.

241. When it is concrete and stratified in different colours it is called *agate* The white and pearl grey translucent agates are called *chalcedony*, the blood red *carnelian*.

242. The common *fire flints* are silex, containing 2 per cent. of water and 1 of alumina. *Tripoli* is silica in fine grains, combined only by their mutual

adhesion, produced by compression. *Sandstone* is quartz sand agglutinated by a calcareous or siliceous cement.

243. CHLORIDE OF SILICON, $SiCl_3$, is a liquid which boils at 122°, and is heavier than water. Its vapour has SG = 5·939, water decomposes it thus :—

$$SiCl_3 + 3HO = SiO_3 + 3HCl.$$

244. This compound is prepared by transmitting a current of dry chlorine over a mixture of silica and carbon in a stoneware retort C, *fig.* 122, heated in a

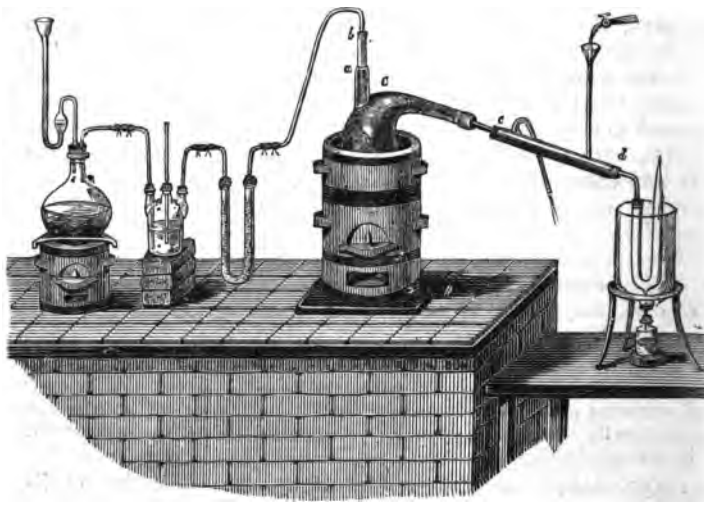


Fig. 122.

furnace. It is condensed in a U-shaped tube, immersed in a freezing mixture. A porcelain tube *b*, of small diameter, passes through *a*, and descends to the bottom of the retort. It is by this tube that the chlorine arrives. The condensation is aided by the straight condensing tube *c d*.

This compound derives interest from its application by Ebelman to produce silicic ether.

245. FLUORIDE OF SILICON, SiF_3, is a colourless gas, which should be collected over mercury, being immediately decomposed by water. Its SG = 3·57. It diffuses thick acid fumes in humid air.

Its composition corresponds to that of silicic acid, fluorine taking the place of oxygen. It extinguishes bodies in combustion, and does not attack glass. It is liquified by the combination of cold and pressure. It is solidified by the cold produced by evaporating in a vacuum a mixture of liquid nitrous oxide and sulphuret of carbon ; potassium decomposes it at a red heat.

Its action on water constitutes one of the most important points of its history.

Absorbing a considerable quantity of that liquid it forms a precipitate of gelatinous silex, and produces a corresponding quantity of hydrofluoric acid, which combining with the undecomposed fluoride forms hydrofluosilicic acid. Thus:—

$$3SiF_3 + 3HO = SiO_3 + \overbrace{2SiF_3,3HF}^{\text{Hydrofluosilicic acid.}}$$

246. PREPARATION. By heating in a glass flask, *fig.* 123, equal parts of fluorspar CaF, and pounded glass, with 6 or 8 parts of highly concentrated sulphuric acid. The silicic acid of the glass parts with its oxygen, which combines with the calcium of the fluor-spar, the resulting lime combining with the sulphuric acid, and the fluorine combining with the silicon, thus:—

$$\overbrace{3CaF}^{\text{Fluor spar.}} + SiO_3 + 3SO_3 = 3(CaO,SO_3) + SiF_3.$$

247. HYDROFLUOSILICIC ACID, $2SiF_3$, $3HF$, has a strong acid taste, and is uncrystallisable. Its most remarkable property is its power of producing in the solutions of the salts of potash, a gelatinous precipitate of the hydrofluosilicate of that alkali, which is scarcely soluble in water. It is often used to detect the salts of potash, or to decompose a salt the acid of which it is desired to isolate. It forms with an alkaline base such as baryta, an insoluble compound, which can be separated by filtration, while the acid of the salt remains free in the liquor.

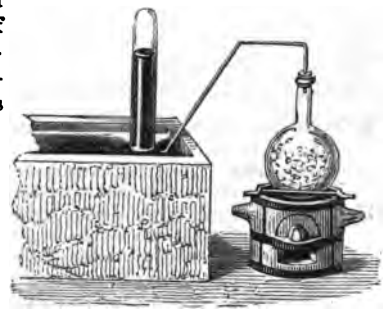


Fig. 123.

It also serves to distinguish the salts of baryta from those of strontia. The former produce with this acid a salt scarcely soluble in water, while the latter are not precipitated.

248. SULPHURET OF SILICON, SiS_3, analogous in composition to silicic acid and the fluoride, is obtained by the action of the sulphuret of carbon on a mixture of silica and carbon. It is solid, but little volatile, and occurs in long brilliant needles. It is decomposed by water at common temperatures:—

$$SiS_3 + 3HO = SiO_3 + 3HS.$$

CHAPTER X.

CLASSIFICATION OF THE METALLOIDS.—TABLE OF BINARY COMPOUNDS.

249. CLASSIFICATION OF THE METALLOIDS. The following classification of the non-metallic elements, the principal of which have been here described, has been proposed by Dumas, and is taught in the French schools.

When the chemical properties of the metalloids are considered collectively, it will be perceived that hydrogen stands apart from the rest. It is *electro-positive* in relation to all the others. It forms with oxygen two compounds, water and the binoxide, both of which are absolutely neutral or indifferent, while among the oxygen compounds of each of the others, there is always at least one acid.

Leaving hydrogen then apart as constituting a class itself, the other metalloids, among which the French chemists include arsenic and tellurium, may be distributed in 4 families as follows :—

I. FLUORINE, CHLORINE, BROMINE, AND IODINE. These manifest strong affinity for hydrogen, with which they all form strong acids of like composition. The other compounds have numerous analogies. Those which are crystalllsed are isomorphous.

II. SULPHUR, SELENIUM, TELLURIUM, AND OXYGEN. They form with hydrogen either weak acids or neutral compounds. The analogies between the compounds of sulphur, selenium, and tellurium are numerous, but oxygen, which in some respects is closely related to sulphur, differs from it completely in this, that it is *electro-negative*, while the other members of the group are *electro-positive*, with relation to chlorine, bromine, and iodine.

III. NITROGEN, PHOSPHORUS, AND ARSENIC. They form with hydrogen gaseous compounds, which have like composition, NH_3, PH_3, and AsH_3. The first is a strong base, and the combinations of the other two are isomorphous.

IV. BORON, SILICON, AND CARBON. The first has not yet been combined with hydrogen, while the second and third have not been *directly* combined with it, although the compounds of carbon and hydrogen are so numerous. The first two form with oxygen, chlorine, and fluorine; compounds which are closely analogous.

Carbon, however, is distinguished not only from boron and silicon, but from all the other metalloids by several properties. Thus its chlorides are not decomposed by water, while the chlorides of the other metalloids form with water hydrochloric acid, and the different oxacids.

The sulphuret of carbon, unlike those of boron and silicon, is not decomposed by water.

250. TABLE OF BINARY COMPOUNDS. In the following table is presented a synopsis of the binary compounds formed by the metalloids with each other, grouped according to their common

constituent, and including arsenic and tellurium, in accordance with the French chemists, from whom the classification is taken.

Oxygen Compounds.

1°. *Neutr*

Water ..... HO
Oxygenated Water .. HO_2
Nitrous Oxide ..... NO
Nitric Oxide. ..... NO_2
Oxide of Phosphorus P_2O
Carbonic Oxide .... CO

2°. *Acids.*

Nitric ..... NO_5
Nitrous ..... NO_4
Hyponitrous ..... NO_3
Chloric ..... ClO_5
Chlorous ..... ClO_3
Hypochloric ..... ClO_4
Hypochlorous ..... ClO
Perchloric ..... ClO_7
Bromic ..... BrO_5
Iodic ..... IO_5
Periodic ..... IO_7
Sulphurous ..... SO_2
Sulphuric ..... SO_3
Hyposulphurous .... S_2O_2
Dithionic ..... S_2O_5
Trithionic ..... S_3O_5
Tetrathionic ..... S_4O_5
Pentathionic ..... S_5O_5
Selenious ..... SeO_2
Selenic ..... SeO_3
Tellurous ..... TeO_2
Telluric ..... TeO_3
Phosphoric ..... PO_5
Phosphorous ..... PO_3
Hypophosphorous .. PO
Arsenious ..... AsO_3
Arsenic ..... AsO^5
Carbonic ..... CO_2
Boracic ..... BO_3
Silicic ..... SiO_3

Hydrogen Compounds.

1°. *Neuters.*

Phosphuret (gaseous) PH_3
„ (liquid) . PH_2
„ (solid) .. P_2H
Arseniuretted ..... AsH_3
Protocarburetted .... C_2H_4
Bicarburetted ..... C^4H_4

2°. *Acids.*

Hydrochloric ..... HCl
Hydrobromic ..... HBr
Hydriodic ..... HI
Hydrofluoric ..... HF
Hydrosulphuric .... HS
Hydroselenic ..... HSe
Hydrotelluric ..... HTe

3°. *Basic.*

Ammonia ..... NH_3

Nitrogen Compounds.

Chloride ..... NCl_3
Iodide ..... NI
Sulphuret ..... NS_2
Nitride of Boron .... BN
Nitride of Phosphorus ..... PN_3

Chlorine Compounds.

Protochloride of Sulphur ..... S_2Cl
Deutochloride do. .. SCl
Protochloride of Phosphorus .. .. PCl_3
Chloride of Arsenic .. $AsCl_3$
Protochloride of Carbon CCl
Bichloride ditto .... CCl_2
Sesquichloride of Carbon ..... C_4Cl_6
Perchloride ditto .... CCl_3
Chloride of Boron .. BCl_3
Chloride of Silicon .. $SiCl_3$

Fluorine Compounds.

Fluoride of Boron ..... BF_3
Fluoride of Silicon ..... SiF_3

Sulphur Compounds.

Subsulphuret of Phosphorus ..... P_2S
Protosulphuret do. .. PS
Trisulphuret do. .... PS_3
Pentasulphuret do. .. PS_5
Persulphuret do. .... PS_{12}
Subsulphuret of Arsenic ..... AsS_2
Trisulphuret do. .... AsS_3
Pentasulphuret do. .. AsS_5
Persulphuret of Arsenic ..... AsS_{18}
Sulphuret of Carbon CS_2
Sulphuret of Boron . BS_3
Sulphuret of Silicon . SiS_3

Cyanogen Compounds.

Cyanogen ..... $Cy=C_2N$
Cyanic Acid ..... CyO
Fulminic Acid .... Cy_2O_3
Cyanuric Acid ..... Cy_3O_3
Hydrocyanic Acid .. HCy
Chloride of Cyanogen (gaseous) ..... $CyCl$
Ditto (liquid) ..... Cy_2Cl_2
Ditto (solid) ..... Cy_3Cl_3

CHAPTER XI.

GENERAL PROPERTIES AND CLASSIFICATION OF THE METALS.

251. ALL the metals, except mercury, are solid at common temperatures. Mercury is liquid.

The metals generally have a peculiar appearance, characteristic of them, called *metallic lustre*. They lose this when pulverised.

They are all opaque, except when reduced to extremely thin leaves, in which state some of them, gold for example, are partially translucent.

Their colour is generally a whitish grey; gold, copper, and titanium being exceptions, the first being yellow, and the other two reddish.

They are generally without odour. Nevertheless tin, copper, iron, and lead, exhale a disagreeable odour, quite perceptible in workshops.

They are generally tasteless; yet some, iron and tin for example, have a peculiar and disagreeable savour.

With the exception of potassium, sodium, and lithium, they are all heavier than water.

The mechanical and physical properties of the metals, such as their SG, hardness, ductility, malleability, tenacity, and conductibility for heat and electricity, are explained in special treatises on physics.*

252. Oxygen enters into combination directly, by mere elevation of temperature, with all the metals, except gold, platinum, palladium, rhodium, and iridium. Water is decomposed, with the agency of heat, by the metals, except gold and platinum. Its decomposition is sometimes determined by the presence of an acid, which forms a salt with the oxide of the metal.

253. The relative force of the affinities of the metals for oxygen is estimated by the three following tests:—

1. The direct action of oxygen upon them, the affinity being stronger the lower the temperature at which combination takes place.
2. The action of heat upon their oxides, the affinity being stronger the higher the temperature necessary to produce decomposition.
3. Their power to decompose water, either by immediate contact, or by the influence of acids.

254. The classification of the metals is based upon their relative affinities for oxygen, determined by these tests. They have been thus grouped in the six following classes:—

255. FIRST CLASS. *Potassium*, *sodium*, *lithium*, *barium*, *strontium*, and *calcium*.

* See Handbook of Nat. Phil.; also, Nat. Phil. for Schools.

These absorb oxygen at common temperatures; their oxides are not decomposed by any attainable heat, and only with difficulty by the contact of bodies having strong affinities for oxygen. They decompose water at common temperatures, disengaging hydrogen.

256. SECOND CLASS. *Glucinum, aluminum, magnesium, zirconium, thorium, yttrium, cerium, lanthanium, didymium, manganese, uranium, pelopium, niobium, erbium,* and *terbium.*

These absorb oxygen at a somewhat elevated temperature, and their oxides are generally as difficult of reduction as those of the first class. They decompose water only at temperatures varying from 200° to 400°, and in some cases only at a red heat.

257. THIRD CLASS. *Iron, nickel, cobalt, zinc, cadmium, chromium,* and *vanadium.*

These absorb oxygen only at a very high temperature. Their oxides are not decomposed by heat, but easily reduced by hydrogen, carbon, and carbonic oxide. They decompose water only at a red heat, or by the aid of acids.

258. FOURTH CLASS. *Tungsten, molybdenum, osmium, tantalum, titanium, tin,* and *antimony.*

These decompose water at a red heat, but not by the influence of acids. But, having a strong tendency to acidification, they decompose it under the influence of strong bases, such as potash.

259. FIFTH CLASS. *Bismuth, lead,* and *copper.*

These decompose aqueous vapour slowly, at a very elevated temperature. Their oxides are not reduced by heat.

260. SIXTH CLASS. *Mercury, silver, rhodium, palladium, ruthenium, platinum,* and *gold.*

These do not decompose water, and their oxides are reduced by heat.

261. In general it may be observed, that the metals of the first class form with oxygen the strongest bases, those of the second, less energetic bases, and some, acids. Among those of the third class are metals having several oxides, some of which are bases and others acids. Those of the fourth class give chiefly acids.*

262. A classification is sometimes adopted and referred to, based upon the characters of the oxides, according to which the metals are distributed in 4 groups, denominated :—

I. THE ALKALINE METALS. *Potassium, sodium,* and *lithium.*
II. THE ALKALINE-EARTHY. *Calcium, barium,* and *strontium.*
III. THE EARTHY. *Aluminum, magnesium, glucinium, circonium, yttrium, erbium, terbium, thorium, pelopium, niobium, cerium, lanthanium, didymium.*
IV. METALS PROPER. All the remaining metals.

263. THE METALLIC OXIDES, being binary compounds of the metals and oxygen, may be grouped in 4 classes, as follows :—

1. Basic oxides.
2. Acid oxides or metallic acids.
3. Indifferent or neutral oxides.
4. Saline oxides.

* This classification is that of Thenard, modified slightly by Regnault.

264. THE BASIC OXIDES belong to the metals of the first class. They have the properties of neutralising the acids, rendering the syrup of violets green, restoring the blue to litmus reddened by acid, and rendering turmeric brown.

265. THE ACID OXIDES neutralise bases with which they form salts, and often redden litmus.

266. THE INDIFFERENT OXIDES combine with neither acids nor bases.

The binoxides of barium, calcium, manganese, and lead, are examples of this class.

267. THE SALINE OXIDES result from the combination of two oxides of the same metal, one of which plays the part of an *acid*, and the other of a *base*, forming therefore a *salt*.

Ex.: The red oxide of manganese, Mn_3O_4, may be regarded as a combination of Mn_2O_3 and MnO, and the sesquioxide of lead Pb_2O_3 of PbO_2 and PbO, the first playing the part of an acid, and the second that of a base.

268. PREPARATION OF THE OXIDES. When the metallic oxides are not found native, they may be prepared in the laboratory by various processes, of which the following are the principal :—

1°. By the direct action of oxygen, either pure or as a component of atmospheric air, upon the metal, raised to a temperature more or less elevated.

2°. By the action of oxidating bodies, such as nitric acid, which impart one or more of their equivalents of oxygen to the metal.

3°. By the calcination of metallic salts, by which they are reduced to oxides.

4°. By precipitating soluble metallic salts by potash, soda, or ammonia. The alkali takes the acid, and leaves the base, which is the oxide isolated.

269. ALLOYS are combinations of metals with each other. These in general are not mere mixtures, as might at first be supposed, but true chemical compounds, their properties often differing completely from those of the constituent metals.

In their general properties alloys are similar to the metals. Thus they are opaque, possess metallic lustre, and conduct heat and electricity.

An alloy generally differs from its constituents in colour, hardness, sonorousness, malleability, and ductility. Hardness, and consequently sonorousness, is generally increased by alloy. The varieties of bell metal are all alloys. Malleability and ductility are usually impaired by alloy. Alloy favours brittleness, that of two brittle metals is always, and that of a brittle and ductile metal generally, and that of two ductile metals often brittle. The density of an alloy always differs from the mean density of its constituents, being sometimes greater and sometimes less, a circumstance which shows that the metals are not merely mixed but chemically combined.

Fusibility is greatly augmented by alloy; platinum, which is almost infusible by a blast furnace, forms a very fusible alloy with zinc or arsenic.

When one of the metals is mercury, the alloy is called an *amalgam*. The silvering of looking-glasses is an amalgam of tin. An amalgam of zinc and tin

is used to promote the action of electrical machines. An amalgam of gold is used in gilding.

Alloys of tin and lead constitute solder. An alloy of antimony, copper, and bismuth constitutes pewter. A mixture of tin, lead, and bismuth forms an alloy which melts below 212°. Type metal is an alloy of lead and antimony. Alloys of copper and tin constitute bronze and bell-metal. Copper and zinc in different proportions yield brass, tombac, dutch-gold, and pinchbeck.

CHAPTER XII.

GENERAL PROPERTIES OF SALTS.

270. UNDER the general denomination of *salts* chemists have included several classes of compounds differing much from each other.

In its original signification the term was applied to compounds of an acid and a base, which more or less neutralised each other. If the acid completely efface the characteristic properties of the base, and the base equally efface those of the acid, the neutralisation is complete, and the compound is called a *neutral salt.* But if the influence of the acid predominate, so that the basic properties are more than effaced, it is called an *acid salt,* and if, on the other hand, the base predominate so that the acid properties are more than effaced, it is called a *basic salt.*

271. Acid salts are sometimes called *super-,* and basic *sub-salts.*

272. But, as has been already stated, the term salt is also applied to a series of binary compounds which result from the reaction of an hydracid upon an oxide, the result of which is a binary compound and water, as when hydrochloric acid acts upon soda, the result of which is chloride of sodium and water—

$$NaO + HCl = NaCl + HO.$$

The chloride of sodium resulting from this reaction iscommon salt, from which salts in general have taken their name.

273. These binary compounds, which include all the metallic chlorides, iodides, bromides, fluorides, cyanides, and sulphurets, possess in as high a degree the characteristic saline characters as the oxy-salts. As already stated, they are denominated *haloid salts.*

274. The metalloid, with which the metal of an haloid is combined, is called a *salt radical.* Thus the radical of common salt is chlorine.

275. THE AMMONIACAL SALTS formed with an hydracid would appear at first view not to come within the class of haloid salts, since the reaction does not result in a binary compound and water. Thus, if hydrochloric acid act on ammonia, the two compounds combine integrally, just as sulphuric acid combines with soda, and the result is the compound expressed by NH_3, HCl, and called,

according to the general principles of nomenclature, *hydrochlorate of ammonia*, being the substance commonly known as sal ammoniac.

But chemists have generally adopted a different view of this compound, and one which would bring it within the class of haloid salts. If the acid be admitted to be decomposed, and to give up its hydrogen to the ammonia, so as to form the compound NH_4, then the composition of sal ammoniac would be expressed thus, NH_4, Cl and it would be the chloride of the compound NH_4. If the compound NH_4 were a metal, the sal ammoniac would be its chloride, and would be an haloid salt corresponding to the chloride of sodium.

It is not in the case of the ammoniacal salts of the hydracids only that this compound, NH_4, plays the part of a metal. The ammoniacal salts of the oxacids present it performing a like part. In all these it is not ammonia, but its hydrate, NH_3,HO, which enters into combination with the acid. Thus the sulphate of ammonia is not NH_3, SO_3, but NH_3, HO, SO_3. But the compound, NH_3, HO, is regarded not as the hydrate of ammonia, but as the oxide of the compound NH_4, and is accordingly written NH_4O, and the sulphate is regarded as the sulphate of the oxide of the compound NH_4, and is written NH_4O, SO_3.

How completely the compound NH_4 in all these cases plays the part and discharges, as it were, the functions of a metal, will be still more apparent if the formulæ representing its compounds be presented in juxtaposition with the corresponding compounds of the metals, and for this purpose we shall express NH_4 by Am.

Metal	K	Na	Am
Oxide	KO	NaO	AmO
Chloride	KCl	NaCl	AmCl
Sulphate	KO, SO_3	NaO, SO_3	AmO, SO_3

Thus the formulæ for the compounds of the metals potassium and sodium are converted into those for the compounds of Am, by the mere substitution of Am for the K or Na.

Chemists generally have accordingly admitted NH_4 provisionally among the metals under the name of *ammonium*, so that the *hydrochlorate of ammonia* is the *chloride of ammonium*, the *sulphate of ammonia* the *sulphate of the oxide of ammonium*, and so on.

This compound has not been left in a state altogether hypothetical, although it has never been isolated. If a salt of ammonia be deposited on a drop of mercury, and put in connection with the negative pole of a voltaic battery while the mercury is in connection with its positive pole, the mercury will be dilated to many times its original volume, will become almost solid, and will retain its metallic aspect. This is regarded as an amalgam of mercury and ammonium. This amalgam, which is crystalline, has properties altogether different from those of mercury.

This and other analogies are regarded by most chemists as grounds for inferring the actual existence of the compound metal NH_4, the failure of

attempts to obtain it isolated being ascribed to its tendency to separate into ammonia and hydrogen.

276. Another class of compounds included under the common name of salts, are those composed of two binary compounds having a common constituent, which have the relative properties of an acid and a base. Thus a compound of the sulphurets of two metals related in this manner is called a *sulpho-salt*, and a similar compound of two chlorides is called a *chloro-salt*.

277. DOUBLE SALTS are produced by the combination of two oxy-salts having a common acid. Thus, for example, the compound formed by the sulphates of potash and alumina, is called a *double sulphate of potash and alumina*, and is the substance familiarly known as *alum*.

An oxide is often combined with an oxy-salt, as, for example, in the sub-sulphates, and subnitrates of mercury and iron, or with an haloid salt, as in the oxychlorides of calcium and mercury.

A double salt is sometimes formed by the combination of an oxy-salt with a haloid salt, as, for example, the nitrate of silver with the cyanuret of mercury.

278. GENERAL PROPERTIES. Salts are almost all solid. Their colour varies with their base. The alkalies, the earths, and certain metallic oxides, form with colourless acids colourless salts. Most of the metallic oxides, however, form coloured salts. A coloured acid gives in general a similarly coloured salt.

279. The taste of salts, generally characteristic, depends most frequently on the base. Thus the salts of magnesia are bitter, those of alumina sweet and astringent, those of lead sweet and styptic. In some cases the taste follows the acid, as, for example, in the case of the sulphites, sulphurets, and cyanurets. Certain acids are capable of producing a taste completely contrary to that of the base. Thus the citrate of magnesia has an agreeable flavour of lemonade, while its base is intensely bitter.

280. Salts in general are crystallisable by one or other of the processes already explained § 45. Few salts have any odour. The carbonate of ammonia (smelling salts) is a striking exception.

Salts have very various affinities for water.

281. DELIQUESCENCE is the gradual dissolution of a salt by moisture attracted by it from the air. Salts which are deliquescent have a strong affinity for water.

282. WATER OF CRYSTALLISATION is the water absorbed by a salt when it is crystallised by evaporation, and which it retains so long as it remains in the crystallised state. This water is so completely absorbed by the crystals that it is not manifested by any moisture upon them, so that notwithstanding its presence the salt may be perfectly dry. The quantity of water of crystallisation may amount to more than half the weight of the salt.

283. AQUEOUS FUSION takes place when a salt is dissolved by heat in its water of crystallisation. The water of crystallisation can always be expelled by heat. No salt can retain its water of crystallisation at a red heat.

284. EFFLORESCENCE is the process by which a salt is reduced to a powder when its water of crystallisation evaporates by mere exposure to the air.

285. WATER OF CONSTITUTION is so combined with a crystallised salt that it cannot be separated from it without decomposing the salt.

286. IGNEOUS FUSION is the process by which a salt is fused after it has lost its water of crystallisation.

287. DECREPITATION is a peculiar crackling noise produced by a salt when exposed to heat. This has been generally ascribed to the sudden expansion of water included between the crystals. That this is not the sole cause is proved by the fact, that some salts perfectly dried still decrepitate. It is probable, therefore, that one of the causes is the unequal expansion of the crystals, arising from the absence of conductibility.

288. Salts in general are decomposed by the voltaic pile, the acid going to the positive, and the base to the negative pole.

289. SOLUBILITY. Salts can be dissolved in liquids, the liquid being called a *solvent*. The solvent most universal is water, and when a salt or other body is said to be more or less soluble, it is generally meant to refer to water as the solvent. Alcohol, ether, the essential oils, sulphuret of carbon, and other liquids are, however, also frequently used as solvents, bodies which are insoluble in some being soluble in others.

290. SATURATION. The proportion of a body which is soluble in any proposed solvent is sometimes unlimited, but more frequently the contrary. A solvent is in general capable of dissolving only a certain limited proportion of a body, and if more be immersed in it, it will either subside or be suspended without being dissolved.

A liquid in which a body is dissolved, is called a *solution* of that body; and if the quantity dissolved be all that the solvent is capable of dissolving, the solution is said to be *saturated*.

The solubility of a body in a liquid is estimated by the proportion necessary to produce saturation.

Ex.: Sulphuric acid is soluble without limit in water. Water is capable of dissolving three times its weight of sugar, and not more. Water is saturated by 36 per cent. of its weight of common salt.

291. Solubility varies with the temperature of the solvent. In most cases it increases, but in some it decreases, with the temperature,—examples of this will be found as the student advances. If a solvent be saturated at a high temperature, by a body whose solubility increases with the temperature, the body in solution will be precipitated as the solution cools, the solvent at each point of temperature retaining in solution just the proportion which saturates it.

Ex.: The solubility of Glauber salts (sulphate of soda) in water, increases rapidly with the temperature. At 32° water is saturated by 5 per cent., while at 103° it will dissolve 42½ per cent. of this salt. If therefore water saturated at 103°, be made to cool gradually down to 32°, the salt will be gradually precipitated until no more than 5 per cent. is dissolved.

If, on the contrary, the solubility decrease with the increase of temperature, the precipitation will take place as the temperature rises.

292. Heat is generally either developed or absorbed by the dissolution of salts in water. It is developed, and the temperature rises, when anhydrous salts capable of forming hydrates are dissolved; but is absorbed, producing a fall of temperature, by salts which already contain all their water of crystallisation.

293. A solution saturated with one salt will often dissolve another, or even two, or more; sometimes in this case, a part of the salt originally dissolved is deposited.

294. The water of crystallisation often varies with the temperature at which the crystals have been deposited.

Thus, borax, crystallised at common temperatures, contains 10 equivalents of water. Crystallised at temperatures above 160°, it contains only 5.

295. In all chemical researches, the reactions of acids and bases upon salts are phenomena of great importance. We shall therefore here briefly state the general principles which have been established in relation to them.

296. Action of Acids. Acids produce various effects upon saline solutions.

For brevity, let B A be the salt in solution, B being its base, and A its acid. Let A′ be the acid which is made to react upon it. If A′ be identical with A, in some cases no reaction will be manifested, but in others B A, if it be a neutral, will be converted into an acid salt, and if it be a basic, will be converted into a neutral salt.

Ex.: Silicic acid has no reaction on silicate of potash. Nitric acid produces the dissolution of nitre, without combining with it. Sulphuric acid converts the sulphate of potash into the bisulphate, and acetic acid converts the subacetate into the acetate of lead.

When A′ is different from A, in some cases no reaction ensues, in others combination takes place, giving B A A′, and in others decomposition and substitution, B A being converted into B A′, and A being liberated.

297. Berthollet's Laws. The phenomena of the decomposition of salts by acids have been generalised by Berthollet, who has ascertained the following laws:—

1°. The salt B A is decomposed by A′, when A′ is more fixed than A. 2°. When A′ forms with B a compound either insoluble, or less soluble than B A. 3°. When A is insoluble, or nearly so, while A′ is soluble. 4°. But if A and A′ be both gaseous, and endowed with

feeble and nearly equal affinities, that which is present in greatest quantity will take effect.

298. Ex.: 1. Let B A be carbonate of potash, and A′ sulphuric acid. The reaction will be—

$$KO,CO_2 + SO_3,HO = CO_2 + HO + KO,SO.$$

Ex.: 2. Let B A be nitre, and A′ sulphuric acid. Then—

$$KO,NO_5 + SO_3,HO = NO_5,HO + KO,SO_3.$$

Ex.: 3. Let B A be sulphate of potash, and A′ silicic acid. Then—

$$KO,SO_3 + SiO_3 = KO,SiO_3 + SO_3.$$
$$\text{or, } + SO_3 + O.$$

In this last example the effect of SiO_3, which is a weak acid, is owing to its stability, it being undecomposable by great heat, § 235.

Ex.: 4. Let B A be nitrate of baryta, and A′ sulphuric acid:—

$$BaO,NO_5 + SO_3,HO = BaO,SO_3 + NO_5,HO.$$

Ex.: 5. Let B A be acetate of potash, and A′ carbonic acid:—

$$\overbrace{KO,C_4H_3O_3,HO}^{\text{Acetate of potash.}} + CO_2 = KO,CO_2 + \overbrace{C_4H_3O_3,HO}^{\text{Acetic acid.}}$$

The solvent in this case must be alcohol.

Ex.: 6. Let B A be silicate of potash, and A′ sulphuric acid,—

$$KO,SiO_3 + SO_3,HO = KO,SO_3 + SiO_3,HO.$$

Ex.: 7. Let B A be stannate of potash, and A′ sulphuric acid,—

$$KO,SnO_3 + SO_3,HO = KO,SO_3 + SnO_3,HO.$$

299. Action of bases. Let B A be the salt, and B′ the base acting upon it. If B′ be identical with B, in some cases there will be no reaction; in others, there will be mere solution; but in others B A, if it be a neutral, is converted into a basic salt, and if it be an acid into a neutral salt.

300. Ex.: Baryta has no effect on its sulphate. Potash dissolves in nitre. The oxide of lead reduces the neutral to the subacetate, and potash reduces the bisulphate to the sulphate.

301. Berthollet's laws. Decomposition will take place: 1°. When B′ is more fixed than B. 2°. When B′ forms with A a salt which is insoluble, or nearly so. 3°. When B′ is soluble, and forms a soluble salt with A, while B is insoluble. 4°. When B′ saturates A more effectually than B.

302. Ex.: 1. Let B A be sulphate of ammonia, and B′ potash:—

$$NH_3.HO,SO_3 + KO = KO,SO_3 + NH_3 + HO.$$

Ex.: 2. Let B A be sulphate of potash, and B′ baryta:—

$$KO,SO_3 + BaO = BaO,SO_3 + KO.$$

Ex.: 3. Let B A be sulphate of magnesia, and B′ potash:—

$$MgO,SO_3 + KO = KO,SO_3 + MgO.$$

Ex.: 4. Let B A be nitrate of copper, and B′ oxide of silver:—

$$CuO,NO_5 + AgO = AgO,NO_5 + CuO.$$

303. Action of salts on each other. If between B A and

B′ A′ there be a reaction, the result will be either a double salt, or reciprocal decomposition.

If the acids A and A′ be identical, a double salt may be formed, in which the two bases B and B′ are combined with the common acid.

Ex.: Let B A be sulphate of alumina, and B′ A′ sulphate of potash. The composition of the double salt is, therefore—

$$\overbrace{3Al_2O_3,SO_3}^{\text{Sulphate of alumina.}},\ KO,SO_3 + 24HO.$$

which always contains 24 equivalents of water.

304. If the acids and bases be different, the reaction will produce mutual decomposition, thus :—

$$BA + B'A' = BA' + B'A.$$

305. Laws of Berthollet. *When the salts* B A *and* B′ A′ *are exposed to a heat which will not decompose their constituents, mutual decomposition will ensue, if* A *can form with* B′ *a less-fixed salt than* B A *or* B′ A′.

Ex.: 1. Let B A be hydrochlorate of ammonia, and B′ A′ carbonate of lime. The reaction is—

$$NH_3,HCl + CaO,CO_2 = NH_3,HO,CO_2 + CaCl.$$

In this case the carbonate of ammonia is less fixed than the hydrochlorate.

Ex.: 2. Let B A be sulphate of baryta, and B′ A′ chloride of calcium :—

$$BaO,SO_3 + CaCl = CaO,SO_3 + BaCl.$$

In this case the chloride of barium is more fusible than that of calcium.

306. *When* B A *and* B′ A′, *by interchange of their acids and bases, give a salt which is insoluble or nearly so, these salts, being in solution, will be mutually decomposed, the least soluble of the resulting salts being precipitated.*

Ex.: Let B A be the sulphate of soda, and B′ A′ the nitrate of baryta: the reaction will give—

$$NaO,SO_3 + BaO,NO_5 = BaO,SO_3 + NaO,NO_5.$$

In this case the sulphate of baryta being insoluble is precipitated.

307. A general method of preparing all the insoluble salts is deducible from the preceding law. The salts of potash and soda and the nitrates being all soluble, when it is desired to prepare an insoluble salt, a salt of potash or soda will supply the acid, and a nitrate will give the base.

Ex.: If it be desired to obtain the carbonate of lead, let the two salts put in solution be carbonate of soda and nitrate of lead, carbonate of lead will be precipitated :—

$$NaO,CO_2 + PbO,NO_5 = PbO,CO_2 + NaO,NO_5.$$

308. The same principles are applicable, not only to soluble salts, which by interchange can produce an insoluble compound, but to all salts which by mutual decomposition can produce a new salt, less soluble than either.

309. ACTION OF SOLUBLE ON INSOLUBLE SALTS.—DULONG'S LAW. *The soluble carbonates decompose, both by fusion and solution, all the insoluble salts, of which the oxide forms with carbonic acid an insoluble salt.*

All the carbonates, except those of potash, soda, lithia, and ammonia, being insoluble, a soluble carbonate will react on the insoluble salts, decomposing them, and will form insoluble carbonates with their bases, while their acids will produce, on the contrary, soluble salts with the alkaline base.

The acid of the salt being therefore in solution, it will be easy to determine its nature; and by dissolving the insoluble carbonate in nitric acid, the metallic oxide of the proposed salt can be ascertained. It is found that a large excess of the carbonate of potash or soda is necessary to effect the complete decomposition of an insoluble salt, and that the mixture should be boiled for several hours.

EX.: Let the insoluble compound which it is required to identify by this method, be sulphate of baryta, BaO,SO_3. The salt is first pulverised and boiled with 5 or 6 times its weight of carbonate of soda, NaO,CO_2, in 15 or 20 times its weight of water for 2 or 3 hours. The mixture is then poured upon a filter. The carbonate of baryta proceeding from the mutual decomposition of the salts—

$$BaO,SO_3 + NaO,CO_2 = BaO,CO_2 + NaO,SO_3,$$

being insoluble, remains on the filter, and is then well washed. The solution passed through the filter contains, combined with the soda, the sulphuric acid of the sulphate of baryta, together with a considerable excess of the carbonate of soda. This excess of the carbonate of soda is decomposed by nitric acid. The carbonate of baryta resulting from the reaction of the carbonate of soda with the sulphate of baryta, is put in contact with dilute nitric acid, which dissolves it. The nitrate of baryta is thus obtained, the presence of which is easily determined by the usual reagents.

This method of Dulong has therefore the advantage of rendering soluble, and therefore easily recognised, all the salts which are not directly dissolved either in water or in the acids.

310. CHLORIDES are soluble in water, with the exception of that of silver, and the protochloride of mercury; the chloride of lead, however, dissolves sparingly. Those of the metals of the 6th class are decomposed by heat, leaving the pure metal isolated. All the others resist a red heat. They are not decomposed by carbon. Heated with nitric acid, they produce aqua regia. The nitrate of silver is the best reagent to determine their presence. It forms in their solutions a white precipitate, readily collected by agitation in curdled flakes, insoluble in water, scarcely so in the acids, but soluble in ammonia, and assuming a violet colour by exposure to light.

311. NITRATES are soluble in water, and decomposable by heat. They deflagrate when thrown upon incandescent charcoal. They

are decomposed by concentrated sulphuric acid. Heated with hydrochloric acid, they form aqua regia.

To detect in a liquid a minute proportion of nitric acid, let sulphate of protoxide of iron be dissolved in water mixed with sulphuric acid, to which add the liquor to be tested, and plunge in it an iron wire. The solution will become red or brown if a nitrate be present. This colour is caused by the salt of iron dissolving the nitric oxide proceeding from the decomposition of the nitric acid by the iron under the influence of the sulphuric acid.

312. SULPHATES, with the exception of those of baryta and lead, are soluble in water. The least so are those of strontia and lime. With the exception of the alkaline sulphates, and those of magnesia and lead, they are decomposed by heat. They are all decomposed by carbon. The soluble sulphates are especially characterised by the property of forming, in dilute solutions of the salts of baryta, a white precipitate of the sulphate of baryta, which is insoluble in water, and in nitric and hydrochloric acids.

313. CARBONATES, with the exception of those of the alkalies, are insoluble in water. Some, however, such as those of lime and baryta, may be dissolved by the influence of an excess of carbonic acid. Heat decomposes all, except those of potash, soda, and lithia. All without exception are decomposed by the vapour of water. Carbon decomposes all, not excepting those of the alkalies. They are decomposed at a high temperature by the vapour of phosphorus, phosphates being formed and carbon being separated.

The neutral are distinguished from the bicarbonates, by precipitating the salts of magnesia.

The soluble carbonates precipitate most of the metallic solutions.

CHAPTER XIII.

POTASSIUM.—SODIUM.—BARIUM.—STRONTIUM.—CALCIUM.

POTASSIUM.

314. THIS metal is solid at common temperatures, and has the metallic lustre. When covered with the oil of naphtha, it has the whiteness of silver; but by exposure to the air it is immediately tarnished, assuming a bluish gray colour. It is soft as wax, so that it may be compressed by the fingers; a process, however, which should only be attempted under naphtha, since the metal burns spontaneously in air, at common temperatures. Its SG = 0·865 at 60°. It would therefore float on water.

Next to mercury, it is the most fusible of the pure metals, its point of fusion being 136°. It is volatilised at a red heat, yielding a green vapour. This experiment should be made by

heating the metal in a glass tube by a spirit lamp, and in an atmosphere of nitrogen, to avoid its oxidation by the oxygen of the air.

Potassium has a strong affinity for oxygen, combining at common temperatures with it. If it be touched with a hot wire, it burns with intensity and is oxidised. It is only in air containing more or less moisture, that it oxidises. In dry air, or even in oxygen if quite dry, it can be preserved without alteration. It decomposes water at common temperatures, combining with its oxygen, and liberating its hydrogen. If a morsel of the metal be thrown upon ice, it burns. The hydrogen liberated in these cases is inflamed by the heat developed by the burning metal, and combining with the oxygen of the air, is reconverted into water.

315. If a morsel of potassium be introduced above the column of mercury in a glass tube, like that of a barometer, and with it a drop of water, the water will disappear, the potassium will change its appearance, and the upper part of the tube will be filled with hydrogen gas proceeding from the decomposed water, which will depress the column of mercury.

This metal has also a great affinity for chlorine, in which it will burn. In virtue of these affinities, it is sometimes used in chemical researches, to separate oxygen and chlorine from their combinations. It combines with a great number of the metalloids.

316. PREPARATION. As potassium is never found native in a separate state, it can only be obtained by the decomposition of one or other of its compounds. If mercury be poured into a cavity made in a piece of solid potash, KO,HO and the potash be put in communication with the positive, while the mercury is in connection with the negative pole of a powerful voltaic battery, the potash will be decomposed, the potassium K going to the negative pole and amalgamating with the mercury, while the oxygen is liberated. If the amalgam thus obtained, be submitted to distillation in a small glass retort, the mercury will be volatilised, while the potassium will remain in the retort.

This was the original experiment by which Davy discovered this metal; although processes are now practised, by which it can be obtained with more facility and in greater quantity.

317. Potash yields about 25 per cent. of its own weight of potassium.

318. THE OXIDES OF POTASSIUM are three: 1°. The suboxide K_2O. 2°. The protoxide KO. 3°. The peroxide KO_3. Of these the second alone has importance.

319. POTASH or POTASSA may exist either in the anhydrous state, or as an hydrate. In the former state its composition is KO, in the latter KO, HO.

Anhydrous potash may be obtained by heating 1 equivalent of the hydrate, with 1 equivalent of potassium, when hydrogen is disengaged and anhydrous potash produced:—

$$KO,HO + K = 2KO + H.$$

Anhydrous potash has a great affinity for water, and absorbs the humidity of the air with great development of heat, being converted into the hydrate.

320. THE HYDRATE KO, HO, which is the substance commonly known as potash, is white, caustic, highly alkaline, and of an unctuous consistency. It produces an instantaneous action on the skin, and by its contact with organic substances produces an odour of lye. It decomposes a great number of animal compounds, such as hair, wool, silk, &c., and saponifies fat substances. It fuses below a red heat, and volatilises as a white vapour. It has a great affinity for water, and by exposure to air deliquesces.

321. The potash of commerce often contains 50 per cent of water. The exact quantity can be determined by exposing it to a red heat, which will reduce it to the hydrate KO, HO. The weight it loses is that of the water it originally contained, exclusive of the last equivalent, which cannot be separated by heat alone.

322. The hydrate KO, HO, is distinguished from other hydrates by the denomination of *caustic potash.*

If caustic potash be treated with an anhydrous acid, such as carbonic or boracic acid, its single equivalent of water will be dismissed, and a salt of the acid formed :—

$$KO,HO + CO_2 = KO,CO_2 + HO.$$

Potash dissolves alumina and silica, and therefore attacks glass and porcelain; it is necessary in consequence to concentrate it in silver capsules.

Hydrogen and nitrogen have no action on potash. Chlorine, sulphur, and carbon, as well as a great number of the metals decompose it, combining with the potassium.

A considerable number of metals also decompose it, combining with its oxygen and liberating the potassium. A method of preparing potassium, by the reaction of iron on potash, is founded on this property.

323. USES. It is a most useful reagent, and serves for the preparation of a great number of oxides. It is applied in the dry way to attack the silicates and render them soluble in the acids. In medicine it is used as a cauterising agent. It is also largely employed in the manufacture of glass, soap, and other articles.

324. NATURAL STATE. It is largely diffused in nature, but always in combination with acids. It forms a component of almost all the rocks, and more especially feldspar. It is sometimes found in considerable quantity in the soil of cultivated land. It serves to saturate partially the acid of vegetables, and forms different organic salts which by calcination give carbonate of potash.

325. SALTS. Potash forms an extensive series of salts. By the reaction of the hydracids it forms a series of haloid salts with chlorine, iodine, bromine, and cyanogen.

326. THE CHLORIDE, KCl, a crystallisable salt, is found in abundance in the waters proceeding from the refining of saltpetre, in the ashes of sea-wrack and almost all vegetables, and in soap-manufactories, where it proceeds from the transformation of the soaps of potash into those of soda, by the reaction of common salt on the former.

It is used in the manufacture of alum, and to convert certain salts of soda into those of potash.

327. THE BROMIDE AND IODIDE, KBr, KI, like the chloride, crystallise in cubes. The iodide is deliquescent, fuses below a red heat, diffusing thick fumes. It is employed in medicine in the treatment of goître and scrofulous maladies. It is also used in photography.

328. THE CYANIDE, KCy, like the others, crystallises in cubes. It is isomorphous with the chloride, its crystals are always anhydrous, and it is one of the most virulent of poisons. It has a slight odour of prussic acid, a strong alkaline reaction, is very soluble in water, and almost insoluble in anhydrous alcohol.

In the dry way it reduces a great number of the metallic oxides, and is regarded as one of the most powerful reducing agents. It dissolves most of the oxides and metallic cyanides; a property which has been utilised in the deposition of metals by the methods of electro-chemistry.

In medicine it is sometimes used instead of hydrocyanic acid. Its toxic properties render it a powerful medicine, but it requires to be used with great prudence.

329. THE SULPHURETS are very numerous, but without much importance. The penta-sulphuret, KS_5, enters into the composition of the *liver of sulphur*, employed in medicine in preparing artificial Barège baths.

330. THE OXY-SALTS of potash are extremely numerous. Those which require notice here are the nitrate, chlorate, sulphate, carbonate, and silicate.

331. THE NITRATE, KO, NO_5, commonly known as *nitre* or *saltpetre*, the most important of these salts, is a friable crystallised body, without colour or odour, with a taste, at first saline and cooling, and afterwards pungent and bitter. Its crystals are six-sided prisms, terminated by hexahedral pyramids, and are always anhydrous. Its SG = 1·933. It is unalterable in the air, save when the atmosphere is nearly saturated with moisture, when it deliquesces. It fuses at 572°, and in cooling forms a white opaque mass of vitreous appearance called *mineral crystal*. A red heat decomposes it, liberating 2 equivalents of oxygen, and reducing it to the nitrite :—

$$KO,NO_5 = KO,NO_3, + 2O.$$

At a white heat a further decomposition takes place, the nitrite itself being decomposed. A mixture of nitrogen and oxygen is disengaged, and caustic potash, mixed with a considerable proportion of the peroxide of potassium, remains. This process must not be conducted in vessels of glass or porcelain, which the potash would pierce in a few moments.

Nitre is soluble in water at low temperatures, but much more so as the temperature rises. Water at 120° dissolves its own weight, and at 212°, 2·36 times its weight of the salt.

332. A mixture of nitre and charcoal burns with great brilliancy. The reaction is—

$$2(KO,NO_5) + 5C = 2(KO,CO_2) + 3CO_2 + 2N,$$

so that the nitrate is converted into the carbonate, carbonic acid and nitrogen being dismissed.

333. Sulphur reacts on nitre at a high temperature :—

$$KO,NO_5 + 2S = KO,SO_3 + SO_2 + N.$$

The nitrate is converted into the sulphate, and sulphurous acid and nitrogen are dismissed.

334. Nitre is decomposed, under the influence of heat, by those acids which are more stable than nitric acid, the latter being liberated.

335. PREPARATION. By directly combining nitric acid with potash, or by decomposing the carbonate by the same acid :—

$$KO,CO_2 + NO_5 = KO,NO_5 + CO_2.$$

336. NATIVE SALTPETRE is abundant. It is found chiefly in Egypt, India, America, and Spain, where it crops out from the surface. It is also found in France, in the department of the Seine and Oise.

337. GUNPOWDER. Among the innumerable uses of this salt in the arts and in medicine, one of the most important is its application to the production of gunpowder. This highly explosive compound consists of nitre, charcoal, and sulphur, mixed in slightly different proportions in the different sorts of powder —sporting, blasting, and war powder. The composition also varies within narrow limits, as adopted in different countries and by different manufacturers. The following may be taken as fair average proportions :—

	Sporting.	Blasting.	War.
Nitre	78	62	75
Charcoal	12	18	15
Sulphur	10	20	10
	100	100	100

The great projectile, or balistic, power of gunpowder arises from the sudden conversion of a small volume of the solid powder into a great volume of gas at a high temperature. When the powder is ignited the reaction of its ingredients may be thus stated :—

$$KO,NO_5 + 3C + S = KS + N + 3CO_2.$$

The proportion here assumed, of 1 equivalent of nitre and sulphur to 3 of charcoal, corresponds to the following rates of the components of gunpowder :—

Nitre . . 74·75 Charcoal . . 13·34 Sulphur . . 11·87

which agrees nearly with that of the sporting powder.

It appears, therefore, that by its ignition the powder is converted into sulphuret of potassium, and a large volume of nitrogen and carbonic acid gas.

According to others, the gaseous products of the reaction are carbonic oxide, sulphurous acid, and nitrogen ; thus :—

$$KO,NO_5 + 3C + S = 3CO + SO_2 + N + KO.$$

On this supposition the gaseous volume developed by 136 grains of powder, the volume of which is $\frac{5}{10}$ of a cubic inch, would be, at common temperatures, 236·2 cubic inches. But, as the gases, in exploding, have the temperature of incandescence, this volume would be expanded in a threefold proportion, being, therefore, about 708 cubic inches, or above 2000 times the volume of the powder.

338. CHLORATE OF POTASH, KO, ClO_5, corresponds in composition to the nitrate, the nitrogen of the latter being replaced by chlorine.

It is a white salt, crystallised in symmetrical hexagonal tables, and more rarely in needles. By exposure to heat it is resolved, first, into the chloride and perchlorate KO,ClO_7, and, by a still higher temperature, the perchlorate itself is resolved into the chloride and oxygen. Thus :—

$$4(KO,ClO_5) = KCl + 3(KO,ClO_7) = 4KCl + 24O.$$

In this decomposition the chlorate yields 40 per cent. of its weight of oxygen. This salt is anhydrous and unalterable in air. At common temperatures water dissolves 6 per cent., and at 212° 60 per cent.

It is not precipitated by nitrate of silver. Chloric being an unstable acid, this salt is easily decomposed, and is consequently a strong oxidant. Its solution, mixed with a small quantity of nitric acid, is employed to produce several oxidations.

A mixture of this salt with sulphur or resinous bodies, when moistened with concentrated sulphuric acid, is inflamed. Sulphuric acid decomposes it, disengaging hypochloric acid with a characteristic odour. By this test the presence of minute quantities of the chlorate is ascertained.

339. PREPARATION. By transmitting a current of chlorine through a concentrated solution of potash:—

$$6KO + 6Cl = 5KCl + KO,ClO_5.$$

The chlorine is produced in the usual way in A, *fig.* 124, and transmitted through the gas-washer, B, to the flask, C, containing the potash. The excess of the uncombined gas escapes by the tube *c d*.

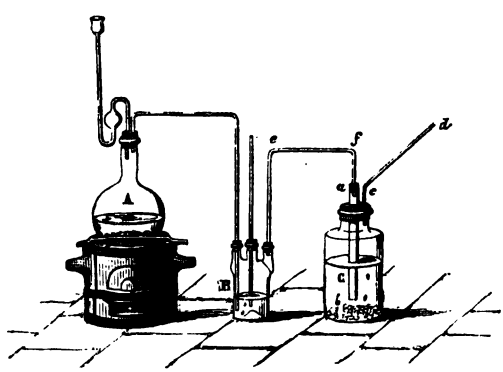


Fig. 124.

340. This salt is chiefly used in the fabrication of lucifer matches.

341. THE SULPHATES of potash are numerous. The best known and most important are the neutral and acid sulphates.

342. THE NEUTRAL SULPHATE, KO,SO_3, is anhydrous, crystallises in prisms with hexahedral pyramidal summits, and is fusible at a high temperature without decomposition. It is soluble in water, its solubility augmenting with the temperature. It is completely insoluble in alcohol and in a concentrated solution of potash. It exists in abundance in sea-wrack and in sea-water. It is used

in medicine as an aperient. Large quantities are consumed in the fabrication of alum and nitre.

343. THE BISULPHATE, or acid sulphate, KO, $2SO_3$, HO, is very acid, reddens litmus, is easily fused, and is dissolved by 2 parts of cold and 1 of boiling water. Exposed to air, its crystals effloresce.

344. THE CARBONATES are three; the neutral, the sesqui-, and the bi-carbonate.

345. THE NEUTRAL CARBONATE, KO, CO_2, known in commerce as *vegetable alkali*, *salt of tartar*, and often called merely *potash*, is a compound of great importance, being largely used in the arts. It has an acrid and slightly caustic taste, and is very soluble in water and deliquescent. Water dissolves at common temperatures its own weight of the salt. It has an alkaline reaction, and crystallises in rhomboidal tables with 2 equivalents of water. The crystallised salt is therefore KO, CO_2, HO. It is insoluble in alcohol, fuses at a red heat, is decomposed by the vapour of water, but not by heat alone. Carbon at a high temperature decomposes it, producing potassium. Lime, in the presence of water, reduces it to the hydrate of potash.

This salt abounds in the vegetable world. When plants are burned the organic acids are destroyed, and the potash remains as a carbonate.

346. THE BICARBONATE, KO, $2(CO_2)$, HO, is obtained by transmitting a current of carbonic acid through a cold solution of the carbonate. The gas is soon absorbed, and the bicarbonate precipitated as a white crystalline substance less soluble than the carbonate. It is collected, pressed, redissolved in water, and finally crystallised by evaporation.

This salt is milder in taste than the carbonate. Its reaction is slightly alkaline. At 212° it is reduced to the carbonate. It is unalterable in the air, and soluble in 4 times its weight of water. When its solution is boiled it is decomposed, being converted first into the sesqui-carbonate, and then into the neutral carbonate.

It is distinguished from the neutral carbonate by not precipitating the salts of magnesia.

In medicine it is used in the treatment of gout and gravel.

SODIUM.

347. This metal has a close analogy to potassium, and was discovered and is prepared by the same process. It has a metallic lustre, and, when freshly cut, the whiteness of silver, but is immediately tarnished by exposure to air. Its SG = 0·972. It fuses at 194°, and is volatilised at a red heat. It is less volatile than potassium, decomposes water at common temperatures, but does not, like potassium, burn when thrown upon water.

The properties of this metal correspond closely with those of potassium. Thus it combines with oxygen in like proportions, forming the suboxide Na_2O, the oxide NaO, and the peroxide NaO_2. The most important of these is the oxide.

348. SODA, or the protoxide NaO, is obtained directly by treating sodium with oxygen. The hydrate of soda, NaO, HO, is obtained in the same manner as that of potash. It is distinguishable from the hydrate of potash, inasmuch as the latter remains deliquescent, while the former, after being liquified, absorbs carbonic acid from the air, and is transformed into the carbonate, which effloresces and falls into powder.

The reaction of the metalloids on soda is the same as on potash.

349. THE CHLORIDE, NaCl, which is the common culinary salt, is familiar to every one as a white substance of an agreeable saline taste. Its SG = 2·13. It is scarcely soluble in alcohol. Water at 60° dissolves 35·8 per cent and at 212° 40 per cent, of it, so that its solubility does not much increase with the temperature. In this respect it is easily distinguished from nitre and other salts. It crystallises in anhydrous cubes, which decrepitate when heated to 300° to 500°. It is fusible at a red heat, and at a higher temperature volatilises, producing white fumes.

When a jet of steam is projected upon a mixture of well dried salt and silica raised to a sufficient temperature, decomposition takes place, and silicate of soda and hydrochloric acid are formed.

$$NaCl + SiO_3 + HO = \overbrace{NaO,SiO_3}^{\text{Silicate of soda.}} + HCl.$$

350. USES. On this reaction is founded the process for glazing common earthenware. A certain quantity of humid salt is thrown into the porcelain oven. The salt is immediately volatilised, and in the presence of the silex of the paste of the ware and the vapour of water produced from its own humidity, it produces the silicate of soda as a vitreous coating which glazes the ware.

Salt has numerous other uses. It serves for the preparation of sulphate of soda, artificial soda, and hydrochloric acid. It is used in the fabrication of bleaching powders. Great quantities are also consumed in domestic economy and agriculture.

351. It is universally diffused in nature, existing in immense quantities in the water of the ocean and of salt springs, and in less proportion in all natural waters, by which it is carried into the sea, where it accumulates. In all inland places which do not freely communicate with the ocean, the pure water escaping by evaporation lets the salt accumulate, so that their water is more salt than that of the ocean, though the rivers which feed them do not contain more than the common proportion of salt. The waters of the Dead Sea (which is, in fact, a lake) are a strong brine.

Salt is also found in abundance in many countries as rock salt, and is obtained from sea-water by evaporation.

352. THE SULPHURETS correspond in their properties and method of preparation to those of potassium.

353. THE NITRATE, NaO, NO_5, called also *cubic nitre*, is a colourless salt, crystallising in anhydrous rhombohedrons. Heat reduces it first to the nitrite and then to anhydrous soda. Its solubility is greater at 32° than at common temperatures. It attracts moisture.

This salt is found native in abundance in Peru.

354. USES. In the fabrication of nitric acid and saltpetre, and as manure in agriculture. A powder consisting of 5 parts of this salt, 5 of charcoal, and 1 of sulphur, which burns with a yellowish-orange flame, is used in pyrotechny.

355. THE SULPHATE, NaO, SO_3, 10HO, better known as *Glauber's salts*, is a colourless salt with a cooling and bitter taste. It crystallises in large four-sided prisms, containing 56 per cent of water. Exposed to air, it effloresces. Heated, it undergoes aqueous fusion, melting in its water of crystallisation, which it loses gradually, and then undergoes igneous fusion without decomposition. Its solubility in water increases from 32°, at which 5 per cent is dissolved, to 90°, at which 50 per cent is dissolved. As the temperature rises above this the solubility decreases to the boiling point, which is 220°.

If 15 parts of this salt be dissolved in 12 of hydrochloric acid a cold is produced sufficient to freeze water.

This salt exists in salt springs. It is prepared by the reaction of sulphuric acid on common salt, thus:—

$$NaCl + SO_3,HO = NaO,SO_3 + HCl.$$

356. USES. It is used in the manufacture of artificial soda and glass, and in medicine as an aperient.

357. THE CARBONATE, NaO, CO_2, 10HO, is a white salt without odour, with an acid and slightly caustic taste, and alkaline reaction. It is very soluble in boiling water, and contains when crystallised 62·69 per cent. of water of crystallisation. By exposure to air it loses a part of this water and effloresces. At 93° it undergoes aqueous fusion; at 212° it loses all its water, and at a red heat undergoes igneous fusion without decomposition. It is not decomposed by heat alone, but a current of steam passed through it at a red heat decomposes it, leaving NaO, HO.

Silica heated with it gives silicate of soda:—

$$NaO,CO_2 + SiO_3 = NaO,SiO_3 + CO_2.$$

Phosphorus, lime, baryta, strontia, and magnesia decompose it.

358. PREPARATION. Formerly this salt was manufactured from certain marine plants, such as the *fucus*, the *sea-wrack*, and also from some maritime plants, such as the *Salsola soda* and the *Salicornia Europæa*. These processes have, however, been nearly superseded by the method of preparing the salt artificially by decomposing sulphate of soda with chalk (carbonate of lime) and charcoal. The reaction is—

$$\underbrace{2(NaO,SO_3)}_{\text{Sulphate of soda.}} + \underbrace{3(CaO,CO_2)}_{\text{Carbonate of lime.}} + 9C = \underbrace{2(NaO,CO_2)}_{\text{Carbonate of soda.}} + \underbrace{2CaS,CaO}_{\text{Oxy-sulphuret of calcium.}} + \underbrace{10CO}_{\text{Carbonic oxide.}}.$$

The 2 equivalents of sulphuret of calcium combine with 1 equivalent of lime to form the oxy-sulphuret of calcium, which is completely insoluble in water, the carbonate of soda being alone dissolved in the liquor.

359. Uses. Immense quantities of this salt are consumed in the manufacture of glass and soap. It is also employed in bleaching and dyeing, and in the washing of thread and cloth.

360. The Bicarbonate, NaO, $2(CO_2)$, HO, and Sesquicarbonate, $2(NaO)$, $3(CO_2)$, 4HO, are of subordinate importance. The former is obtained by transmitting a current of carbonic acid through a concentrated solution of the carbonate; and the latter is found native in warm countries, such as Egypt, Mexico, and India, being known under the name of *natron* or *trona salt.*

The bicarbonate is employed in medicine as a remedy for indigestion and for calculus.

361. The Borate, NaO, $2(BO_3)$, 10HO, commonly known in commerce as *Borax*, is found native crystallised in Persia, India, and China. It is sometimes called *tincal* in commerce. It is white, with an alkaline taste and soluble; is soluble in 12 times its weight of cold and twice its weight of boiling water. Exposed to air it effloresces. Heated it swells, loses its water, and is fused into a vitreous mass.

362. Uses. It dissolves several metallic oxides, receiving various tints of colour, which are tests of the oxides in blowpipe analyses. Thus the oxide of cobalt gives it a blue colour, that of manganese violet, and so on.

In the reduction of oxides by charcoal it acts as a flux. It is used also for solders. It enters into the composition of certain sorts of glass, and the glaze of porcelain.

BARIUM.

363. This metal was discovered and is prepared in the same manner as potassium and sodium. It has a yellow colour, fuses below a red heat, and is not volatilised at the highest temperatures. Exposed to the air it absorbs oxygen, and is tarnished. It decomposes water rapidly, disengaging hydrogen, and is converted into baryta,

$$Ba + HO = BaO + H.$$

364. Baryta, BaO, when anhydrous is a spongy grayish-white substance with an acrid taste, which is poisonous. It is extremely caustic, and renders the syrup of violets green. It is infusible in a forge fire, but may be fused by the oxy-hydrogen blowpipe. It is not decomposed by heat. Exposed to air, it attracts moisture and carbonic acid, and is reduced to powder. Water dissolves 5 per cent. at common temperatures, and 10 at 212°. When dissolved in boiling water, the crystals obtained in cooling are the hydrate, BaO, 10HO.

Chlorine decomposes it, liberating the oxygen, and producing chloride of barium. Sulphur reacts upon it under the influence of heat, producing the sulphate or hyposulphate or the sulphuret of barium, according to the temperature. Phosphorus in like manner produces the phosphate or phosphuret.

Baryta acts on organic matter, disorganising it like potash and soda.

365. The chloride BaCl, 2HO, has an acid and disagreeable taste, and, like all the salts of baryta, is poisonous. At common temperatures water dissolves 43·5 per cent, and at 212°, 77 per cent. It is insoluble in hydrochloric acid.

It is used in the laboratory as a reagent to detect sulphuric acid and the sulphates.

It is prepared by dissolving the carbonate in hydrochloric acid :—

$$BaO,CO_2 + HCl = BaCl + CO_2 + HO.$$

366. The Nitrate, BaO, NO_5, crystallises in regular octohedrons, unalterable in air and always anhydrous. Water dissolves 5 per cent at 32°, and 35 at 212°. It is insoluble in alcohol and hydrochloric acid.

It is used to prepare baryta, and to precipitate free sulphuric acid and the sulphates.

367. The Sulphate, BaO, SO_3, commonly known as *heavy spar*, is found in abundance in masses, and with veins of silver, antimony, copper, and mercury. Its SG = 4·7. It is almost insoluble in water, and completely so in nitric and hydrochloric acids. Boiling concentrated sulphuric acid sensibly dissolves it. It is precipitated from this solution by adding water to it. It is not decomposable by heat. It is fusible at a high temperature.

Uses. It is used as a flux in copper-foundries, enters into the composition of certain sorts of glass, is mixed sometimes with white lead, and is used in the laboratory to prepare other salts of baryta.

368. The Carbonate, BaO,CO_2, occurs native, and is then called *witherite*. It is colourless, and crystallises in rhomboidal prisms. Its SG = 4·29. It is completely insoluble in water, and can be obtained by double decomposition by treating a salt of baryta by a soluble carbonate. By the heat of a forge-fire it is decomposed, dismissing its carbonic acid.

STRONTIUM.

369. This metal is obtained and was discovered in the same manner as all the former. It has a golden yellow lustre, absorbs oxygen from the air, and is transformed into strontia. It decomposes water like barium. Its SG = 2·54.

370. Strontia, SrO, is a grayish spongy solid, like baryta, which attracts humidity and carbonic acid from the air. Dissolved in water, it produces the hydrate SrO,10HO, which, being heated,

is reduced to SrO,HO, which is not decomposable by heat. It is prepared by decomposing the nitrate SrO,NO_5, by heat, in a porcelain retort.

371. The Chloride, SrCl,6HO, may be obtained by the reaction of the chloride of calcium CaCl on the sulphate SrO,SO_3. It crystallises in water in long needles, of the composition SrCl,6HO, which are reduced by heat to the anhydrous chloride SrCl. Water at common temperatures dissolves 66 per cent., and at 212°, 125 per cent. It is soluble in alcohol, the solution burning with a fine carmine flame, by which it is distinguished from the chloride of barium, the flame of which does not differ from that of alcohol.

It is almost insoluble in concentrated hydrochloric acid.

372. The Nitrate, SrO,NO_5, crystallises in regular octohedrons. Water at common temperatures dissolves 20 per cent., and at 212°, 100 per cent. It is insoluble in alcohol; a property which supplies the means of separating it from the nitrate of lime which is soluble in alcohol. It is decomposed by heat.

373. The Sulphate, SrO,SO_3, called in mineralogy *celestine*, crystallises in rhomboidal prisms. Its SG = 3·89, it is white, and insipid. Water dissolves only 1 part of this salt in 3000 or 4000, yet the amount dissolved is sensible; the solution precipitates the soluble salts of baryta, proving that the sulphate of baryta is still less soluble than that of strontia.

This salt accompanies native sulphur in the solfataras of Sicily.

It serves to prepare the other salts of strontia.

374. The Carbonate, SrO,CO_2, exists native, and is known as *strontianite*. It crystallises in right prisms, is colourless with SG = 3·65. It is decomposed by a high temperature, and is insoluble in water. It may consequently be obtained by double decomposition by treating a soluble salt of strontia with a soluble carbonate.

CALCIUM.

375. This was discovered and is prepared like the preceding metals. It is white, with metallic lustre, and when heated in air is converted into lime.

376. Lime, which is the protoxide of calcium, CaO, was known to the ancients, having been used in all their mortars.

Lime is white, caustic, very alkaline, with SG = 1·3. It renders the syrup of violets green. If a piece of lime be immersed for a moment in water and then withdrawn it will become hydrated, and a development of heat will take place, which may raise the temperature to 570°, and produce the hissing noise which usually accompanies the sudden production of steam. The heat developed by the contact of lime with water is sufficient to ignite gunpowder.

377. SLAKED LIME is lime which has been reduced to powder by the absorption of water. Anhydrous lime is distinguished as *quick lime*. Slaked lime is the hydrate CaO,HO, quick lime being CaO.

378. MILK OF LIME is water holding lime in suspension, and having the consistency of cream.

379. FAT LIME is lime moistened with water, so as to have a pasty consistency.

380. LIME WATER is an aqueous solution of lime. At common temperatures a saturated solution of lime contains only 1 part by weight of lime to 778 of water. At 212°, such a solution contains a still less proportion of lime, 1 part to 1300 of water.

It follows, therefore, that if lime water be boiled, a certain proportion of the lime will be separated, and will render it turbid.

381. Sugar combines with lime and renders it more soluble. Lime, in whatever state it may be, absorbs carbonic acid from the air, and is converted into the carbonate, becoming hard and compact like limestone. It is on this property that the efficiency of mortar depends.

382. Lime having a strong affinity for carbonic acid, which always exists in a greater or less proportion both in air and water, is never found pure in nature, but always combined with that acid, forming the carbonate, which is presented in the varieties of chalk, marble, Iceland spar, arragonite, and so on. The shells of oysters and of mollusca generally, consist of the carbonate of lime almost in a state of purity. Lime is also a constituent of plaster of Paris, of the bones of animals, and of silicious rocks, besides the vast strata of limestone. Most vegetables contain it combined with organic acids.

383. PREPARATION. Lime, CaO, is usually prepared by decomposing one or other of its salts by heat, which can always be effected, inasmuch as lime itself cannot be so decomposed. Chalk or limestone is the native carbonate generally used for this purpose. It is submitted to calcination in a kiln or furnace, varying in form and magnitude according to the purpose to which it is applied. On a small scale in the laboratory, it may be prepared with the apparatus shown in *fig.* 125, where *a* is the furnace in which the limestone is placed, and *f* a receiver, in which the carbonic acid disengaged is collected.

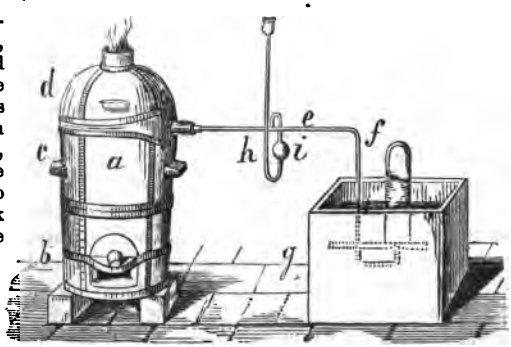


Fig. 125.

On a larger scale the stone is calcined in kilns of various forms, the gas being allowed to escape. A section of a kiln of intermitting action is shown in *fig.* 126. This being filled, and the calcination completed, the operation is suspended until it is discharged and refilled. A kiln of constant action is shown in vertical section in *fig.* 127. The kiln is discharged through orifices *o*, *o'*, near its base, other openings *e* admit air to support the combustion. The

Fig. 126.

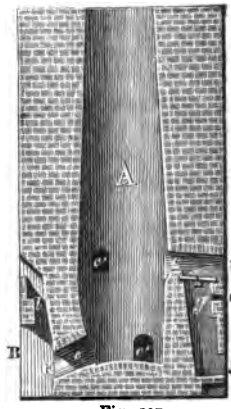


Fig. 127.

entire capacity of the kiln A is filled with limestone. The lower strata being first calcined are discharged, and a corresponding quantity of stone deposited at the top; and so the process is continued.

384. Uses. It is the base of mortars, is employed in tanning, in the purification of gas for illumination, in the preparation of potash and soda, in the fabrication of stearine candles, and sugar. It is used also in agriculture.

385. Chloride of calcium, CaCl, is found in the water of the ocean, of rivers, fountains, and wells. It is prepared by transmitting a current of chlorine over lime at a red heat, or by the action of hydrochloric acid on marble. This compound is white, has a bitter taste, and crystallises in 6-sided prisms. These crystals retain 4 equivalents of water in a vacuum.

It has a great affinity for water, and is one of the most deliquescent bodies known. Water at 60° will dissolve about 1·5 times its weight of this chloride. A saturated solution boils at 368°. As already often mentioned, its great affinity for water causes it to be employed for drying gases, and for absorbing water from certain liquids which hold it in solution.

When it is anhydrous, it is easily dissolved in alcohol. It combines with ammonia, forming the compound $CaCl,4NH_3$. It cannot, therefore, be used to dry ammoniacal gas.

386. Fluoride of calcium, CaFl, commonly called *Fluor*

spar, is a well known mineral. It enters in a small proportion into the composition of the bones and the enamel of the teeth. It has sometimes a yellowish, sometimes a violet colour, and in rare cases is colourless. It crystallises in cubes with SG = 3·1. Under the action of heat it is phosphorescent. Certain varieties called *chlorophane* emit a green light after calcination. It fuses at a high temperature, and crystallises in cooling. Being insoluble, it may be obtained by double decomposition in precipitating a soluble fluoride by a salt of lime. It serves to prepare hydrofluoric acid, and the fluorides of silicon and boron.

Fluor spar having often very beautiful colours, is used for ornamental objects, such as cups and vases. It is used as a flux, especially in the treatment of the ores of copper.

387. CHLORIDE OF LIME is the name given to a mixture of the salt of lime called hypochlorite, CaO, ClO, with the chloride of calcium, CaCl.

This is the bleaching powder of commerce, which is used on an immense scale in the art of bleaching. It is white, amorphous, and pulverulent, with an odour resembling, but sensibly different, from that of chlorine. Water dissolves it largely. Treated with acids, its chlorine is liberated, and hence arises its great bleaching power. Let us suppose that the acid is SO_3. The reaction will then be—

$$CaO,ClO + CaCl + 2SO_3 = 2(CaO,SO_3 + 2Cl),$$

so that the whole is resolved into the sulphate of lime, and free chlorine.

Chemists, however, are not altogether in accordance as to the nature of the reaction.

388. PREPARATION. A current of chlorine is transmitted through the milk of lime, the reaction being—

$$2Cl + 2CaO = CaO,ClO + CaCl.$$

Care should be taken that an excess of lime be always present, otherwise the hypochlorite might be transformed into the chlorate. The mass diluted with water and decanted, gives a concentrated solution of the chloride. The operation may be conducted in Woolf's apparatus, *fig.* 53.

389. USES. Besides its application to bleaching cotton and linen, it is also used for bleaching the pulp of which paper is made. It is used as a mordant in dyeing and calico-printing. Also, as a disinfectant in hospitals and dissecting-rooms, where, however, it should be applied in small quantities, since the disengagement of an excess of chlorine would exercise an injurious effect on the organs of respiration.

390. SULPHATE OF LIME is found in nature, both anhydrous and hydrated, the former is CaO,SO_3, and the latter $CaO,SO_3,2HO$. The anhydrous sulphate in mineralogy is called *anhydrite*, and the

hydrate is the substance called *gypsum*, and more familiarly known as *plaster of Paris*. These are both found in abundance in the triassic formation associated with rock salt, and in the inferior tertiary rocks.

The gypsum near Paris is found in the marly beds above the coarse limestone which supplies the building stone. This gypsum is a fresh-water deposit, as appears by the river shells found in it.

391. This salt occurs in large transparent tabular crystals, easily cleaved, and having the form of right quadrangular crystals with rhomboidal base, and are usually grouped in the form of a lance.

392. GYPSOUS ALABASTER consists of these crystals in an opaque state. This must not be confounded with the more valuable calcareous alabaster.

393. Sulphate of lime is almost tasteless, with a faintly bitter savour. It is colourless, and not decomposed by heat. It is slightly soluble in water, 1000 parts dissolving 2 of the sulphate. The solubility does not vary with the temperature. In concentrated sulphuric acid, it forms the bisulphate $CaO,2(SO_3),HO$, which is decomposable by water. It is completely insoluble in alcohol. Its SG = 2·31. It is dehydrated at 400°.

394. The hydrate, $CaO,SO_3,2HO$, has the hardness of stone, but when dehydrated, it becomes pulverulent. But again in contact with water it is hydrated, and recovers its hardness. In virtue of this property it is employed as a cement.

395. STUCCO is plaster of Paris soaked with gelatine, or a solution of gum. It is susceptible of polish so as to assume the appearance of marble. Fragments of marble are often mixed with it before solidification, which are then polished with the stucco. As stucco does not resist humidity, it can only be employed in the interior of buildings.

396. CARBONATE OF LIME, CaO, CO_2, is one of the most important calcareous compounds, as well on account of its vast abundance in nature as of its innumerable uses in the arts. It is presented as Iceland spar, arragonite, coarse limestone, building stone, marble, chalk, alabaster, lithographic stone, and in an infinite variety of other states.

The pure carbonate is white, but the slightest admixture of foreign matter suffices to colour it. The veins and colours of marble are ascribed to the admixture of metallic oxides.

Its hardness is subject to great variety. Marble is harder than common limestone, and the latter is harder than chalk. At a red heat it is resolved into lime and carbonic acid. But if it be heated in a closed vessel, or gun-barrel, it will be fused without decomposition, and will present, on being slowly cooled, the consistency and properties of marble. Artificial marble has been produced in this way.

It is insoluble in water, and may therefore be obtained by double decomposition by the reaction of a soluble carbonate and a salt of lime. Carbonic acid easily dissolves it, producing a bicarbonate soluble in water.

397. This property explains several natural phenomena. When water, holding in solution carbonic acid, passes through carbonate of lime, it transforms it into the bicarbonate, which is dissolved, but being very unstable, it soon loses half its carbonic acid, and is restored to the state of carbonate, which being insoluble, is deposited in the solid state. Hence arise the calcareous deposits which often obstruct waterpipes, the incrustations in steam-boilers, and the crystalline deposits called *stalactites* and *stalagmites*. When water holding carbonic acid in solution infiltrates through a bed of limestone, it dissolves the carbonate as explained above, and passing through the clefts of rocks which form natural caves or grottoes, it is again reduced to the insoluble carbonate which forms projecting masses on the roofs called *stalactites*, and on the floor called *stalagmites* (*fig.* 128). The portion which drops on the floor before it is decomposed forms the latter, which being directly under the corresponding stalactite they often unite in the middle, as shown in the figure.

Fig. 128.

If various objects, such as fruits, birds' nests, &c., be exposed to the action of certain mineral waters, which hold in solution the bicarbonate of lime, incrustations will be formed upon them, so that they will be converted into what are popularly called *petrifactions*. The most celebrated springs of this sort are those of *Carlsbad*, which produce a calcareous deposit of great beauty which is used in the fabrication of ornamental objects. The waters of San Filippo in Tuscany, and of Saint Allyre in Auvergne, have a like property.

The calcareous tufas employed in building have the same origin.

398. PHOSPHATE OF LIME is of three sorts, the basic, $3CaO,PO_5$; the neutral, $2CaO,HO,PO_5,3HO$; and the acid, $CaO,2HO,PO_5$. The first has most interest, as it enters into the composition of the animal skeleton, and is thence called *bone-phosphate*.

This phosphate is white, insoluble in water, soluble in acids, and of a gelatinous consistency. It is obtained by pouring chloride of calcium, CaCl, into phosphate of soda, $3NaO,PO_5$.

The inorganic part of the bones contains 80 per cent. of this phosphate.

CHAPTER XIV.

MAGNESIUM.—ALUMINUM.—MANGANESE.

MAGNESIUM.

399. A MIXTURE of the anhydrous chloride of magnesium and potassium being heated in a close platinum crucible, the chloride of potassium is produced, and the metal is isolated. The chloride is dissolved out by cold water and the magnesium remains.

400. Magnesium possesses the metallic lustre of silver, and is malleable and fusible at a red heat. Its SG = 1·87. It decomposes water at 86°, is slowly oxidised in humid air, and when heated in oxygen burns, being converted into magnesia. It burns also in air, chlorine and the vapour of sulphur. The acids, even when diluted, dissolve it, disengaging hydrogen.

401. MAGNESIA, MgO, the only oxide of this metal, is prepared in the hydrated state by precipitating a salt of magnesia by an excess of potash, the acid of the salt combining with the potash, and the magnesia being separated.

It is white, pulverulent, without taste or smell, with SG = 2·3. 1 part requires 55,000 parts of boiling water, but rather less of cold water, for solution. Like lime, it is therefore more soluble at low than at high temperatures. It has a feeble alkaline reaction, renders the syrup of violets green, and saturates the acids. In contact with water it becomes MgO,HO, and in contact with humid air, it absorbs at once carbonic acid, and is converted into the carbonate.

It is absolutely infusible at the heat of the strongest furnaces; but can be fused, and even volatilised, by a voltaic pile of 185 elements.

402. USES. It is used in medicine to neutralise the acidity of the stomach, and also as an antidote to acid poisons. It combines directly with arsenious acid to form an insoluble compound, and is consequently applicable as an antidote to that poison.

403. THE SULPHATE, MgO,SO_3, is a white salt of a bitter and saline taste, soluble in water, with which it forms several hydrates, containing 1, 2, 5, 6, 7, and 12 equivalents of water, according to the temperature at which the crystallisation takes place. Submitted to heat it undergoes successively aqueous and igneous fusion and decomposition. It effloresces when exposed in air.

In the presence of water, and at a high temperature, it is decomposed by common salt:—

$$MgO,SO_3 + NaCl = NaO,SO_3 + MgCl.$$

It exists in the water of saline springs at Epsom and at Seidlitz, whence it has been called *Epsom salts* and *Seidlitz salts*.

It is employed in medicine as an aperient.

404. THE CARBONATES OF MAGNESIA are the neutral, MgO,CO_3, which has hydrates containing 3, 4, and 5 equivalents of water, and the basic $4MgO,3CO_2,4HO$, which is the white magnesia of pharmacy. It is prepared by boiling a solution of sulphate of magnesia with carbonate of potash in excess. Carbonic acid is disengaged, and all the magnesia is precipitated in the state of a basic salt.

White magnesia is manufactured on a large scale for medicine. It is formed into large rectangular solid masses. In England and Bohemia it is prepared by precipitating waters which contain the sulphate by an alkaline carbonate.

It is more soluble at low than at high temperatures.

ALUMINUM.

405. This metal is obtained by the reaction of potassium on its anhydrous chloride in the same manner as magnesium is isolated. It has been recently found advantageous to substitute for the chloride, the preparation of which is difficult and troublesome, the double chloride of aluminum and sodium; a compound easily obtained by transmitting chlorine over a mixture of alumina, common salt, and charcoal. It is volatile and fusible, but quite solid when cold.

406. Aluminum is usually grayish, but takes the whiteness of tin when rubbed with the burnisher. Its SG = 2·6. It fuses at a red heat, is ductile, and is not tarnished by exposure to air at common temperatures. At a red heat in pure oxygen it burns brightly, and is transformed into alumina. The heat developed in this combustion is so intense as to fuse the resulting alumina, although it is one of the most refractory bodies known.

407. ALUMINA, Al_2O_3, the sesquioxide of aluminum, and the only known compound of the metal with oxygen, exists in unbounded quantity in nature. It is a constituent of all clays, marls, felspar, mica, and many other minerals. The mineral called *corundum* is pure alumina in a crystallised state. When corundum is colourless it is called *hyalin*, or *white sapphire*; when red it is the *oriental ruby*; when blue it is the *sapphire*; when green the *oriental emerald*; when violet the *oriental amethyst*. These several varieties of crystallised alumina constitute precious stones of a value often comparable to that of the diamond.

408. *Emery*, used for polishing glass and metals, is a variety of corundum which contains a considerable proportion of iron. It is used to polish glass, metals, and certain stones, such as *agate*.

409. Alumina is usually prepared by calcining ammoniacal alum, $(NH_3,HO,SO_3)\ (Al_2O_3,3SO_3),24HO$, at a red heat. All the con-

stituents of this salt are thus disengaged, except the alumina, which remains perfectly pure.

Thus prepared it is a white, tasteless, coherent mass, which adheres to the tongue. It is infusible in the furnace, but yields to the oxy-hydrogen blowpipe, and becomes very fluid. It cannot, like silica, be drawn into threads. By fusing it with traces of chromate of potash, artificial rubies were obtained by M. Gaudin.

It is not decomposable by heat, is insoluble in water, but is dissolved by the acids when it has not been calcined. It is completely soluble in potash and soda. One of its characteristic properties is manifested by treating it with nitrate of cobalt, when a fine blue compound is produced. It is decomposable by chlorine and the other metalloids.

Exposed in air it does not absorb carbonic acid, and it has no known carbonate.

410. HYDRATED ALUMINA is obtained by precipitating a salt of alumina by carbonate of soda. It retains its water with tenacity, giving it up only to a red heat.

411. USES. Agriculture derives great advantage from the property by which alumina condenses and retains water. It is thus that the soil, of which alumina is always a chief constituent, retains that degree of humidity which is useful to vegetation.

Hydrated alumina combining with colouring matters forms the class of insoluble compounds called *lakes*. Salts of alumina are employed in dyeing, as mordants. Combining with certain bases it manifests the properties of an acid. Thus it forms aluminates with potash and soda. Spinelle is an aluminate of magnesia, MgO, Al_2O_3.

412. CHLORIDE OF ALUMINUM, Al_2Cl_3, is solid, volatile, and of a light yellowish colour. It is very soluble in water, and diffuses white fumes in air. In contact with water it becomes hydrated, hissing like red-hot iron. It is very soluble in alcohol.

413. THE SULPHATES OF ALUMINA are very numerous, the most important being, $Al_2O_3,3SO_3$; $2(Al_2O_3),3SO_3$, and $3(Al_2O_3),3SO_3$. The first, considered as the neutral sulphate, crystallises in thin flexible plates of a pearly lustre; it is very soluble in water, but scarcely so in alcohol. It has a sweetish astringent taste, and acid reaction. It contains 18 equivalents of water, and, heated, undergoes aqueous fusion and then swells, being decomposed, and leaving alumina as a residue.

414. ALUMS. The salifiable bases consisting of metallic protoxides MO, and sesquioxides M_2O_3, being combined with sulphuric acid, give two classes of neutral sulphates, one having the composition MO,SO_3, and the other $M_2O_3,3SO_3$. The following are examples of these classes :—

MO,SO_3	$M_2O_3,3SO_3$
KO,SO_3	$Fe_2O_3,3SO_3$
NaO,SO_3	$Al_2O_3,3SO_3$
MnO,SO_3	$Cr_2O_3,3SO_3$
FeO,SO_3	$Mn_2O_3,3SO_3$

The general name of *Alums* is given to the class of double sulphates produced by the combination of a sulphate of the first class with one of the second. Thus the alum of alumina and potash, commonly called potash alum, is (KO,SO_3) $(Al_2O_3,3SO_3)$, the alum of potash and chrome is (KO,SO_3) $(Cr_2O_3,3SO_3)$, and so on.

The alums all crystallise in cubes or octahedrons.

All the alums contain 24 equivalents of water, with the exception of those of ammonia, which contain 25, a circumstance which arises from the fact that the ammoniacal salts all contain 1 equivalent of water of constitution.

415. POTASH ALUM, (KO,SO_3) $(Al_2O_3,3SO_3),24HO$, the most important of the class, is a white salt of astringent taste and acid reaction, with SG = 1·71. Water at 32° dissolves 3·29 per cent., and at 212°, 3·57 per cent. It effloresces slowly. It fuses at 198°. At a higher temperature it loses its water and swells into the form of a large opaque mushroom, which is employed in medicine as a caustic under the name of *calcined alum*.

If it be cooled at 198°, its crystals are transparent. In this state it is called *Rock alum*.

At a high temperature it is completely decomposed, giving a residuum of alumina and sulphate of potash. At a still higher temperature the sulphate is also decomposed.

416. PREPARATION. It is prepared by calcination from various alum stones found in different parts of Italy, Pozzuoli, near Naples, Zolfa, near Civita Vecchia, and elsewhere.

417. USES. In calico printing as a mordant, in the preparation of sheep skins, the sizing of paper, and the clarification of liquids.

418. FELDSPAR is a compound of silicate of alumina with other silicates. *Orthose*, variously denominated *feldspar* and *petunze* is (KO,SiO_3) $(Al_2O_3, 3SiO_3)$; it crystallises in rhombohedral prisms with SG = 2·5, scratches glass, is fusible in a porcelain oven, and yields a milky glass.

419. KAOLIN, or fine potter's earth, when purified, has the composition $SiO_3,Al_2O_3,2HO$.

MANGANESE.

420. This metal is solid, hard, brittle, fixed, and very refractory, of a grayish colour resembling that of cast iron. It has a faint metallic lustre, and is easily worked with the file. Its SG = 8 nearly. It has a strong affinity for oxygen, is oxidised in air, and decomposes water at common temperatures. It should therefore be kept under oil of naphtha, or in a closed glass tube.

421. PREPARATION. By reducing its oxide in a brasque crucible.*

* A crucible lined with a thick coating of powdered charcoal.

422. THE OXIDES OF MANGANESE. These are six :—

Protoxide	MnO
Red oxide	Mn_3O_4
Sesquioxide	Mn_2O_3
Peroxide	MnO_2
Manganic acid	MnO_3
Permanganic acid	Mn_2O_7

423. THE PROTOXIDE, MnO, the base of its principal salts, is anhydrous, greenish, and not decomposable by heat. It easily absorbs oxygen and becomes brown. When heated in air it is converted into the red oxide. It is dissolved by hydrochloric acid without disengaging chlorine.

$$MnO + HCl = MnCl + HO.$$

As hydrate it is white, but even at common temperatures it is rapidly converted into the sesquioxide.

424. PREPARATION. By decomposing a salt of manganese by a solution of potash or soda.

$$MnO,SO_3 + KO,HO = MnO,HO + KO,SO_3.$$

425. THE RED OXIDE, Mn_3O_4, called in mineralogy *Hausmanite*, is found native. It is the most fixed of the oxides, is not altered by heat, and is incapable of forming salts. Borax and glass when fused dissolve it, and acquire the colour of amethyst. It may be regarded as a compound of the protoxide and sesquioxide.

426. THE SESQUIOXIDE, Mn_2O_3 is also found native, being called by mineralogists *braunite* when anhydrous, and *manganite* when hydrated. It has a blackish brown colour, is dissolved without change in some acids, and forms true salts.

427. THE PEROXIDE, MnO_2, the most important of the oxides, serves for the preparation of oxygen and chlorine, and is used in the glass manufacture to whiten glasses coloured by iron oxides.

It is found native in abundance in prismatic crystals or in crystalline radiated masses. When pure and anhydrous, it is called *pyrolusite* in mineralogy.

428. It is decomposed by heat, yielding a third of its oxygen, and being converted into the red oxide.

$$3MnO_2 = Mn_3O_4 + O_2.$$

It is decomposed by hydrochloric acid.

$$MnO_2 + 2HCl = MnCl + Cl + 2HO.$$

Sulphuric acid does not act upon it at common temperatures, but decomposes it when heated.

$$MnO_2 + SO_3,HO = MnO,SO_3 + O.$$

Nitric acid alone has no action on it, but in the presence of organic matter decomposes it.

$$MnO_2 + NO_5 = MnO,NO_5 + O.$$

It decomposes oxalic acid.

$$\underbrace{2(C_2O_3,3HO)}_{\text{Oxalic acid.}} + MnO_2 = MnO,C_2O_3 + 6HO + 2CO_2.$$

It is dissolved by glass and borax, imparting a fine dark violet colour.

429. PREPARATION. By various processes, one of which consists in heating the sesquioxide with the chlorate of potash.

$$6Mn_2O_3 + KO,ClO_5 = 12MnO_2 + KCl.$$

430. Manganic acid, MnO_3, has not yet been obtained in a separate state, for when a manganate is decomposed its acid is also decomposed.

431. When potash is fused with peroxide of manganese and nitre, a body is produced which imparts to water a succession of colours—green, violet, and red, according to the proportion of water in the solution, and which was hence called *mineral chameleon.* This body was ascertained to contain manganic acid.

432. MANGANATE OF POTASH, KO, MnO_3, is very unstable, yielding part of its oxygen to a great number of bodies, being resolved into potash and the sesquioxide. All organic matters destroy it, and consequently it cannot be filtered through paper. An excess of potash gives it stability. A red heat decomposes it.

$$2(KO,MnO_3,) = 2KO + Mn_2O_3 + 3O.$$

In the presence of a great quantity of water it is transformed into the permanganate which is purple, depositing hydrate of the peroxide:—

$$3(KO,MnO_3) + 2HO = KO,Mn_2O_7 + MnO_2 + 2(KO,HO).$$

CHAPTER XV.

IRON.—COBALT.—NICKEL.—ZINC.—TIN.—ANTIMONY.—ARSENIC.

IRON.

433. CONSIDERED in reference to its utility, iron is the most valuable of the metals. Happily, it is provided in such unbounded quantity in nature, and the materials for working it are so abundant, and deposited naturally so close to the metal, that notwithstanding its vast consumption in the arts, its marketable value is low.

It is found in nature sometimes, though rarely, in the metallic state, uncombined with any metalloid. In such cases it is considered to be of meteoric origin; that is, to constitute part of those stones which fall upon the earth, coming from some unknown region of the universe, and are called *meteoric stones*, or *meteorites.* Its ores are oxides, carbonates, and sulphurets. In these combinations it prevails in immense quantity in almost all countries. It is found in a small proportion in every rock and soil, and the

carbonate is held in solution in the water of certain springs, which are thence called *chalybeate waters.*

434. The ores are chiefly, 1, *clay ironstone,* which is a carbonate of the protoxide, and accompanies the coal formations in England and Scotland; 2, *red hæmatite,* a pure peroxide, and

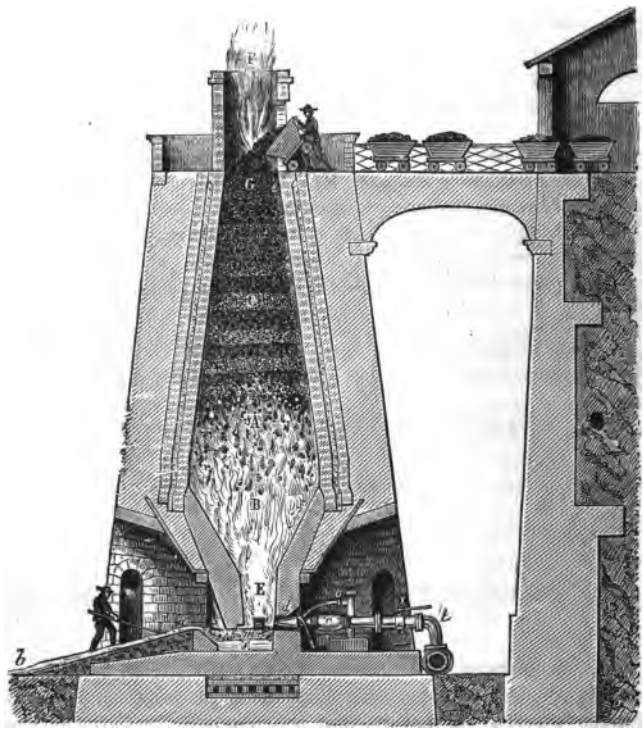


Fig. 129.

brown hæmatite, a hydrated peroxide; 3, black, or magnetic oxide.

435. Extraction. The ores are reduced and the metallic iron separated by subjecting them to a high temperature in furnaces, in which they are laid in alternate layers with coal, lime, and sandstone. The carbon of the coal decomposes the ore, separating the iron. The lime and sand perform the office of a flux, producing a liquid slag, through which the fused iron falls to the lower part of the furnace, from which it is drawn off from time to

time through apertures provided for the purpose. These furnaces are usually constructed on a vast scale of magnitude, the height of the interior, for the reception of the ore and fuel, varying from 50 to 60 feet. A section of such a furnace, showing the manner of feeding it at the top, G, and discharging the reduced iron in fusion at the base, is shown in *fig.* 129. The furnace is blown by three blast-pipes, one of which appears at *t d*, which receive a strong current of air from blowing-cylinders, one of which is shown in section in *fig.* 130, the directions in which the air is

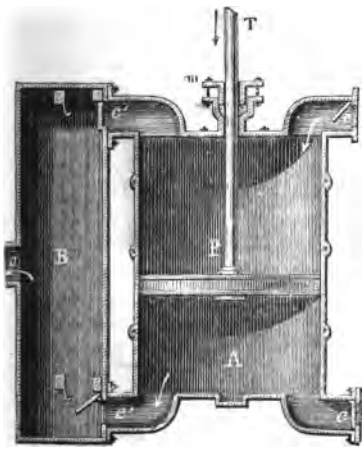


Fig. 130.

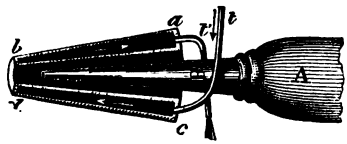


Fig. 131.

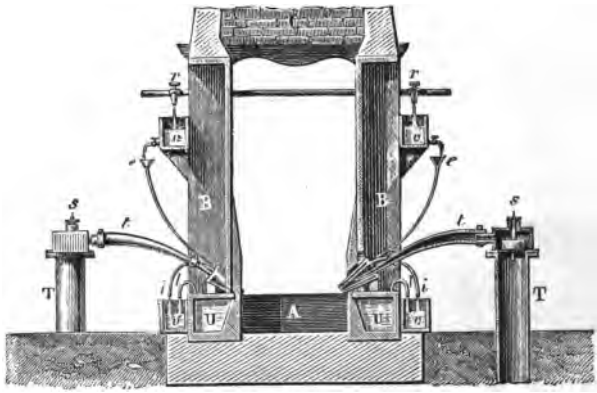
drawn in and driven out by the piston P being indicated by the arrows.* The nozzle of the blast-pipe is prevented from being fused by transmitting around it a current of cold water in the space indicated by the arrows in *fig.* 131. The fused iron received from the furnace is cast in the form of short prismatic pieces, called *pigs*, and the metal in this state is thence called *pig iron.*

Pig iron is never pure, since it always contains unreduced ore and earthy impurities, besides a considerable quantity of charcoal in combination. It is much more fusible and brittle than pure iron, to convert it into which it is again fused in another form of furnace, called a *finery furnace*, where the liquid metal is exposed to strong currents of air, driven in by a series of blast-pipes in connection with blowing-cylinders. A finery furnace is shown in vertical

* See H. B. Nat. Phil., Pneumatics, § 280.

section in *fig.* 132, and in plan in *fig.* 133, where A is the bed of fused metal and *t t t* the blast-pipes, *v v* being the cisterns from which the cold water is supplied to keep the nozzles from being fused.

Fig. 132.



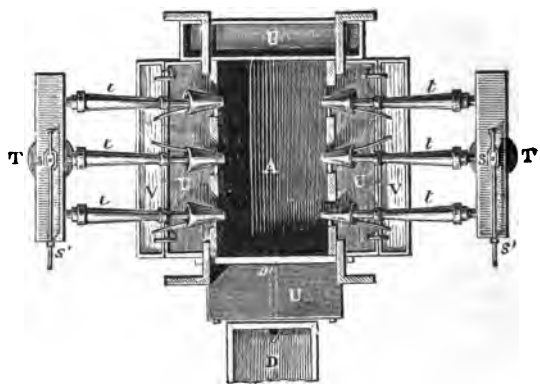


Fig. 133.

By the oxidating power of the air the carbon of the iron is converted into carbonic acid, which escapes as gas, and the silex proceeding from the sandstone into silicic acid, which, combining with a portion of the oxide of the metal, forms fusible silicates, which separate as scoriæ. The mass being agitated, these scoriæ and other impurities rise to the surface. The iron gradually becomes less fusible as the matters which acted as a flux are separated. The heat is gradually augmented until the metal remains

solid at the highest temperature. It is then rendered still more pure and dense under the hammer. One of the forms of sledge

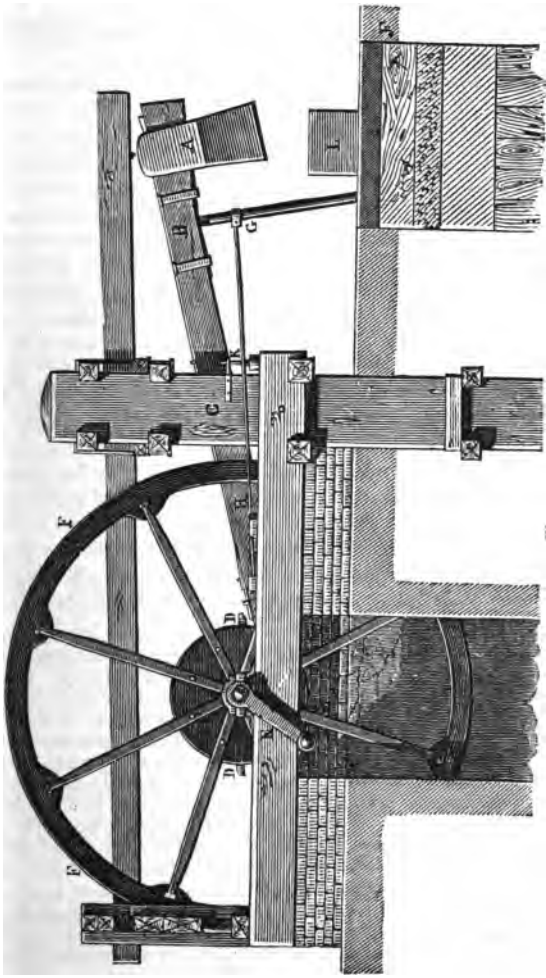


Fig. 134.

hammer used for this purpose is shown in *fig.* 134, where L is the anvil, A the hammer, D D the cams by which it is raised, and F the fly-wheel which equalises the action.*

* See H. B. Nat. Phil., Mechanics, § 657.

436. The metal is not yet chemically pure. To obtain it in that state, the pure oxide is exposed at a red heat to a current of hydrogen, which combining with its oxygen carries off the water thus formed in the state of vapour, the pure metal remaining as a spongy mass.

437. The iron of commerce has a bluish-gray colour, is malleable and ductile, and is the most tenacious of the metals. A wire, the 12th of an inch in diameter, will support nearly a quarter of a ton. It admits of polish, has a faint taste and smell, becomes brittle under the hammer, but recovers its tenacity when annealed.* It is naturally granular, and the quality is better according as the grain is finer and more brilliant. It becomes fibrous when hammered. The fracture of good iron presents a fine, brilliant, and twisted fibre. It it be hammered cold in the direction of its length, or if it be tempered, it again becomes granular.

If fibrous iron be submitted to frequent vibration a molecular action takes place, which determines its crystallisation. It is thus that the bars and chains of suspension bridges, and the axles of locomotives, originally sound and strong, sometimes become brittle.

438. Malleable iron has SG = 7·7, which may be increased to 7·9 by hammering. It is estimated that its point of fusion is 3000°.

439. When iron is raised to a red heat it becomes so soft that it is capable of being reduced to any desired form by percussion or compression. This is a property from which the greatest advantage is derived in its application to the uses of industry.

440. WELDING. When iron is raised to a red heat, it becomes capable of welding, and still more so at a white heat. This is a property from which great advantage is derived in its application to the uses of industry. Two bars or other pieces of the metal, by laying their ends or edges one upon the other, and submitting them to the hammer, can be united in a manner so complete, that the junction shall be as solid as any other part. This process is called *welding*.

441. ROLLING. In virtue of the same property, any desired form can be given to the metal by the hammer, or still more easily and perfectly by *rollers*, which are cylinders of steel, shaped in correspondence with the form to be given to the bar. These cylinders, A B and A′ B′, are mounted, as shown in *fig.* 135, with their axes parallel, and their surfaces nearly in contact, and are kept in uniform revolution by suitable machinery. The grooves on their surfaces are formed in accordance with the shape required to be given to the bar, which being white hot, and therefore soft, is passed between them. The grooves through which it is successively passed, diminish gradually in magnitude, as shown at A A′ and B B′, so that the bars are gradually reduced in their thickness, while they are increased in their length.

It is by such machinery that bar iron, and the rails for railways are manufactured.

442. MAGNETISM is a property of which iron is eminently susceptible.†

* That is, when heated and slowly cooled. See H. B. Nat. Phil., Heat, § 476.

† See H. B. Nat. Phil., Electricity and Magnetism.

443. THE FLINT AND STEEL. When iron strikes a hard body, such as flint, sufficient heat is developed at the point of percussion to render the minute particles of the metal which are struck off, incandescent. They combine with the oxygen of the air, and are converted into one of the oxides of the metal, as may be ascertained by collecting them on paper, placed under the flint.

444. RUST. Iron exposed to humid air is *rusted*, that is, superficially oxidated. The first portion of oxide which is produced forms with the metal under it a voltaic combination, from which a feeble voltaic current results. Thus the humidity of the air is decomposed, its oxygen in the nascent state combining with the metal and increasing the oxidation.

445. The oxidation may be prevented by coating the iron with grease or varnish, or by immersing it in water, having alkalies or alkaline salts in solution, or, in fine, by coating it with zinc. Iron thus prepared with a zinc coating, is called *galvanised iron.*

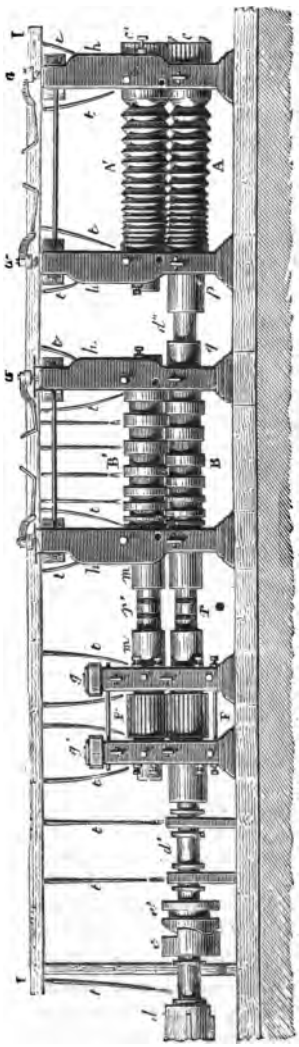


Fig. 135.

446. The compounds of iron with oxygen are four :—

Protoxide	FeO
Magnetic oxide	Fe_3O_4
Sesquioxide, or peroxide .	Fe_2O_3
Ferric acid	FeO_3

447. THE PROTOXIDE, FeO, is a powerful base. Owing to its affinity for oxygen, it is unknown in the uncombined state ; the hydrate, FeO, HO, however exists, and is when pure white. It exists in nature, combined with a great number of acids.

448. THE PEROXIDE, Fe_2O_3, is a feeble base, isomorphous with alumina. It is found native, as specular iron, beautifully crystallised, in Elba and elsewhere, and as *red* and *brown hæmatite.*

449. PREPARATION. The sulphate of the protoxide, calcined, leaves as a residuum this oxide—

$$2(FeO,SO_3) = SO_3 + SO_2 + Fe_2O_3.$$

Thus prepared, it is a fine red powder, known as *colcothar*, and as *jeweller's rouge*, it is also used in painting.

At a white heat it disengages oxygen, and is converted into the magnetic oxide—

$$3Fe_2O_3 = 2Fe_3O_4 + O.$$

The peroxide, therefore, can never be produced by burning iron, since the magnetic oxide alone can bear the temperature produced by the combustion.

This oxide is reduced by hydrogen at a high temperature, producing pure iron:—

$$Fe_2O_3 + 3H = 2Fe + 3HO.$$

Submitted to calcination it acquires great hardness, a quality also found in the native oxide. When polished it is employed, under the name hæmatite, to burnish gold and silver. Colcothar is used to polish glass and several metals.

450. The magnetic oxide, Fe_3O_4, the native magnet or loadstone, is found in the more ancient formations in compact masses, and sometimes, as at Tabey in Sweden, forms entire mountains. Its appearance is metallic, and as its name implies it is highly magnetic. It is crystallised in regular octohedrons. Its SG = 5·09. It constitutes the finest iron ore, the metal it produces being nearly pure. Hence arises the great excellence of the Swedish iron.

451. The hydrate of this oxide is a dark green substance, which by desiccation is reduced to a black powder. It is magnetic, and may be regarded as a combination of the protoxide and sesquioxide.

452. Ferric acid, FeO_3, has not been obtained free, and is only found in combination with bases forming salts having the general composition MO, FeO_3.

453. The Ferrate of potash, KO,FeO_3, may be obtained by transmitting a current of chlorine through a concentrated solution of potash, which holds in suspension the hydrated peroxide—

$$5KO + 3Cl + Fe_2O_3 = 3KCl + 2(KO,FeO_3).$$

The solution of this salt in water has a fine red colour. It is precipitated in the state of black flakes, without decomposition, by an excess of alkali. It is very unstable, being decomposed by mere evaporation in a vacuum, by a slight degree of heat, by the presence of bodies in subdivision, or organic matter, or by the action of the weakest acids. It is thus decomposed:—

$$2(KO,FeO_3) = 2KO + Fe_2O_3 + 3O.$$

The alkalies and hypochlorites render it stable.

454. The ferrate of soda is altogether analogous to that of potash.

455. The soluble ferrates are decomposed by ammonia.

$$2(KO,FeO_3) + NH_3 = N + Fe_2O_3 + 2KO + 3HO.$$

456. The ferrates of baryta, strontia, lime, &c., obtained by double decomposition, are bright red insoluble compounds.

457. The salts of the protoxide have an astringent and metallic taste, and when hydrated their colour is generally greenish, or pale bluish green, but they become almost white, when dehydrated by heat. They have a tendency to become oxidated in air, and their solutions deposit an ochreous precipitate of a salt of the peroxide.

The neutral salts of the sesquioxide have a yellow colour, which becomes darker when the proportion of the base is augmented. Their solutions always redden litmus.

458. THE CYANIDES correspond in composition to the oxides, and are—

Proto-cyanide	$FeCy$
Sesqui-cyanide	Fe_2Cy_3
Magnetic cyanide	Fe_3Cy_4

459. THE FERRO-CYANIDE OF POTASSIUM, $2(KCy), FeCy, 3HO$, better known as the *prussiate of potash*, is largely employed in the arts. In the laboratory it is a most useful reagent for determining a great number of the metals; poured into metallic solutions, it forms precipitates of various colours, in which the 2 equivalents of potassium are replaced by 2 equivalents of the metal which is in solution. The colour of the precipitate indicates the metal.

460. THE FERRID-CYANIDE OF POTASSIUM, $3(KCy), Fe_2 Cy_3$, is an equally useful reagent for detecting the presence of the metals; poured into a metallic solution it produces an insoluble ferrid-cyanide, in which the 3 equivalents of potassium are replaced by 3 equivalents of the metal in solution.

461. PRUSSIAN BLUE, $3(FeCy), 2(Fe_2 Cy_3)$, is a compound of the proto- and sesqui- cyanides of iron. It is prepared by precipitating a salt of the higher oxide by ferrocyanide of potassium.

462. The compounds of sulphur and iron are—

1	Subsulphurets	Fe_2S & Fe_3S
2	Protosulphuret	FeS
3	Sesquisulphuret	Fe_2S_3
4	Bisulphuret	FeS_2
5	MagneticPyrites	Fe_7S_8
6	Persulphuret	FeS_3

463. THE PROTOSULPHURET, FeS, may be obtained hydrated by precipitating a salt of the protoxide by an alkaline sulphuret :—

$$FeO,SO_3 + KS = KO,SO_3, + FeS.$$

It is a black substance, insoluble in water and in the alkalies and alkaline sulphurets. It gives a fine green solution. Exposed to the air it absorbs oxygen, and is converted into the sulphate—

$$FeS + 4O = FeO,SO_3.$$

It is of rare occurrence in nature. It sometimes occurs in coal mines, where it often produces accidents. Being oxidated it developes heat sufficient to ignite coal, from which cause fires have sometimes occurred in mines.

464. THE SESQUISULPHURET, $Fe_2 S_3$, may be prepared by pouring a salt of the sesquioxide into an alkaline sulphuret.

It is found native in combination with the protosulphuret of copper, forming *copper pyrites*, the most abundant ore of copper.

465. THE BISULPHURET, FeS_2, better known as *iron pyrites*, may be prepared by heating with precaution the protosulphuret with half its weight of sulphur. It is of a brass yellow colour, SG = 4·981, and hard enough to strike fire. When calcined in close vessels it loses half its sulphur, and is transformed into magnetic pyrites. It is only attacked by nitric acid, aqua regia, and concentrated boiling sulphuric acid.

466. MAGNETIC PYRITES, Fe_7S_8, or according to some chemists Fe_6S_7, is the most stable of the sulphurets. It occurs in nature, and may be prepared artificially by heating any of the oxides with an excess of sulphur.

467. THE SULPHATE OF THE PROTOXIDE, FeO, SO_3, 7HO, commonly known as *green vitriol*, has a styptic taste, is not poisonous, is soluble in twice its weight of cold and $\frac{3}{4}$ of its weight of boiling water. It crystallises in oblique rhomboidal prisms. Crystallised at 176°, with an excess of acid, it is FeO, SO_3, 3HO, at 212° it is FeO, SO_3, HO. The last equivalent of water is dismissed only at a very high temperature.

Three varieties are known in commerce. The first, a greenish blue, is produced when the salt is crystallised in acid liquors; the second, a pale green, in neutral liquor; and the third, an emerald green, in liquors which contain a great quantity of the sulphate of the sesquioxide.

It is decomposed at a red heat, thus:

$$2(FeO,SO_3) = Fe_2O_3 + SO_2 + SO_3.$$

All oxidants transform it into the sulphate of the peroxide.

468. PREPARATION. By heating iron with dilute sulphuric acid—

$$SO_3,HO + Fe = FeO,SO_3 + H;$$

or by exposing efflorescent pyrites to the air, which, absorbing oxygen, are transformed into the sulphate.

469. THE CARBONATE, FeO,CO_2, may be obtained in crystals, by heating to 300°, in a closed tube, a mixture of carbonate of lime and protochloride of iron.

$$FeCl + CaO,CO_2 = FeO,CO_2 + CaCl.$$

It is insoluble in water, but soluble in an aqueous solution of carbonic acid. Most of the natural ferruginous waters contain this carbonate, dissolved in carbonic acid.

It is found native, crystallised in rhombohedrons, under the name of *spathic iron*. It is considered an excellent source of the metal, and is the ore almost exclusively worked in England.

COBALT.

470. This metal is obtained by reducing its oxide by carbon or hydrogen, or by decomposing its chloride by hydrogen. It is difficult, however, to obtain it pure, since it always retains some traces of iron, nickel, or arsenic. It has sometimes the whiteness

of silver, and sometimes has a reddish gray colour. Its fracture shows a fine grain, like that of steel. Its SG = 8·6. It is as difficult to fuse as iron, and is equally fixed. It does not oxidise in air or water at common temperatures, but oxidises rapidly when the temperature is raised.

It is magnetic, and is dissolved slowly by sulphuric and hydrochloric acids, with the disengagement of hydrogen. Nitric acid has a strong action upon it.

It combines directly with chlorine, sulphur, phosphorus, and arsenic.

471. Its oxides are—

Protoxide	CoO
Sesquioxide	Co_2O_3
Intermediate oxides	Co_3O_4, Co_6O_7

The first alone is important.

472. THE PROTOXIDE, CoO, is obtained anhydrous, as an amorphous, dark-olive powder, by calcining in close vessels the hydrated protoxide. The latter is obtained by heating a salt of cobalt with caustic potash.

The blue precipitate obtained by decomposing the salts of cobalt is a basic salt, and not the oxide, as has been supposed.

The oxide, heated with glass or borax, produces tints of pure blue, which resist the highest temperatures of the porcelain oven. A slight trace of this oxide suffices to give a sensible blue colour. Fused borax coloured by it yields a beautiful dark blue glass. It combines with the alkalies and metallic oxides. Heated with potash in a silver crucible it gives a compound of a fine blue colour, which is decomposed by contact with water.

Under the influence of heat it combines with magnesia, alumina, and the oxide of zinc. With alumina it produces a superb blue, and with zinc a fine green.

This oxide is used in the manufacture of glass and porcelain, to impart a blue colour to the ware.

473. THE SALTS of cobalt have the protoxide as their base. When dissolved in a large quantity of water they have a fine peach red or garnet colour; but when their solution is concentrated, the colour is sometimes blue. The crystallised salts are red. The soluble salts calcined, or the insoluble salts merely dried, may be red, lilac, or blue. Their taste is astringent, and their reaction always acid.

474. THE CHLORIDE, CoCl, is obtained by dissolving the oxide in hydrochloric oxide. Its solution is red; but when it is very acid, or when, after being concentrated, it is heated, it becomes blue. Whenever it is found by concentration and heat to take a green tint, it may be inferred to contain oxide of nickel or of iron.

This property of changing its colour renders it fit for *sympathetic ink*.

475. SMALT is a blue glass, prepared by heating the roasted ore of cobalt with quartzose sand and potash.

The *smalt blue* of commerce is this glass finely pulverised.

NICKEL.

476. This metal, when pure and unmixed with cobalt, is white, unalterable in air, ductile, malleable, and almost as refractory as manganese. Carbon, uniting with it, increases its fusibility. Its SG = 8·279, which is augmented to 8·666 when forged. Heated in oxygen it burns like iron, and is slowly dissolved by the strong acids. It is magnetic, but loses this property by great elevation of temperature.

The properties here stated would render this metal highly valuable if it were more abundant. It is at present used as a component of the alloy called *packfong*, an imitation of silver, consisting of 50 per cent. of copper, 25 of zinc, and 25 of nickel. This alloy is better known as *German silver*.

Nickel is obtained by the reduction of its protoxide in a brasque crucible at a forge fire.

477. THE OXIDES are three, NiO, Ni_2O_3, and a peroxide of unascertained composition. The first alone is of importance.

478. THE PROTOXIDE, NiO, is obtained anhydrous by calcining the nitrate, and hydrated by precipitating a salt of the metal by an excess of potash or soda.

The anhydrous oxide has an ashy gray colour, the hydrate an apple green. It is insoluble in potash and soda, but is dissolved by ammonia, the solution having a beautiful blue colour. It is precipitated from this solution by potash, baryta, and strontia. It may be precipitated in certain cases by ammonia; as when an excess of ammonia is poured into a solution of a salt of nickel, which also contains other metallic salts.

Hydrogen at a red heat reduces this oxide.

479. THE SALTS have the protoxide as their base. Those which are soluble have a fine green colour. The anhydrous salts have a yellow tint. Their taste is sweet at first, then acrid and metallic. They have always a metallic reaction, and are not precipitated by any metal. They are all decomposable by heat, the sulphate being the most refractory.

Organic matters, and chiefly tartaric acid, prevent the precipitation of the protoxide by the alkalies, but do not prevent the precipitation of the salts by the hydrosulphate of ammonia.

480. PREPARATION. The metal is obtained from its native arseniuret, NiAs, which is called *kupfernickel*, and is the most abundant of its ores. An arsenical sulphuret, called *speiss*, which collects at the bottom of the crucibles in which *smalt* is fabricated, is also employed.

ZINC.

481. ZINC, which was known and used in the arts by the ancients, is a solid, bluish-white metal, of lamellous texture. When fused its SG = 6·862, and when rolled 7·215. It has a peculiar quality, by which it greases the file; has little sonorousness; it is soft, but less so than lead or tin. When very pure it may be reduced to thin leaves under the hammer: the zinc of commerce, however, is not so malleable. When cold it cracks when flattened by the hammer; but at 250° to 300° it becomes malleable, and can be forged, laminated, and even wire-drawn. At about 400° it becomes very brittle, and may be pulverised in an iron mortar raised to this temperature. It has but little tenacity, 25 lb. breaking a wire of a line in diameter. It is fusible at about 700°. When slowly cooled it crystallises in hexagonal prisms, and sometimes in rhomboidal dodecahedrons. When fused and poured from a certain height into water it becomes granulated.

The zinc of commerce is never chemically pure, containing about 1 per cent. of other bodies, which are chiefly lead and iron. Carbon, cadmium, copper, and arsenic are sometimes present. Distillation does not completely purify it.

Zinc is not oxidised in dry air. In moist air it becomes invested with a thin coating of oxide, which preserves the metal within from further oxidation.

At about 900° it inflames, burning with a white flame. It decomposes the vapour of water under the influence of heat, being oxidised, and disengaging hydrogen. This decomposition takes place at 370°.

It has been already shown, § 87, that it decomposes water at common temperatures in the presence of acids.

Zinc precipitates from their solutions a great number of metals (copper, tin, antimony); and in a solution of a salt of iron decomposes water.

482. THE OXIDES are Zn_2O, ZnO, and ZnO_2.

483. THE SUBOXIDE, Zn_2O, a blackish gray body, is decomposed under the influence of the acids, and resolved into ZnO and Zn. This oxide has not yet been obtained in a state of purity.

484. THE PROTOXIDE, ZnO, is obtained when the metal is burned in air. It is a fine white powder, which becomes yellow when calcined, but recovers its whiteness when cooled. It is fixed, and not decomposable by heat. It is reduced by hydrogen and carbon. It is a powerful base, and neutralises the acids.

485. The hydrate, ZnO,HO, is obtained by pouring dilute potash into a solution of a salt of zinc. It is soluble in potash, soda, and ammonia, with which it forms saline compounds called *zincates*.

Mixed with drying oils, the oxide of zinc forms a paint called *zinc-white*, which has lately been substituted for *white lead*.

486. THE SALTS of zinc are colourless, and of a styptic, bitter, and nauseous taste, are poisonous, and in small doses used as an emetic. Many have an acid reaction, and are precipitated by none of the metals.

487. THE SULPHURET, ZnS, is obtained by the action of a soluble sulphuret upon a salt of zinc, or of carbon on the sulphate —

$$ZnO,SO_3 + 4C = 4CO + ZnS.$$

It is a light white powder insoluble in water; but is attacked when hot by concentrated hydrochloric acid.

It occurs native as *zinc blende* in dodecahedral crystals, which vary in colour, being sometimes yellow, and sometimes red, brown, or black.

488. THE SULPHATE, $ZnO, SO_3, 7HO$, is white, and when crystallised at common temperatures, contains 7 equivalents of water. Its crystals are prismatic. Boiled in alcohol of 96° it becomes $ZnO,SO_3,5HO$. Other hydrates, with 1 and 2 equivalents of water, are obtained under different conditions, that which is best known being however $ZnO, SO_3, 7HO$.

Water dissolves 40 per cent. of this salt at common temperatures, and 100 per cent. at 212°. It is decomposed by heat, being first reduced to a basic salt, and finally decomposed completely.

489. THE CARBONATE, ZnO, CO_2, is found native in small crystals, stalactites, and amorphous masses. It is called in mineralogy, *smithsonite*, *calamine*, and *zinconise*. It cannot be obtained artificially. It is insoluble in distilled water, but is soluble in water charged with carbonic acid. It forms with the carbonates of potash and soda double salts, whose composition is—

$$(ZnO, CO_2)\ (KO, CO_2);\ or\ (ZnO, CO_2),\ (NaO, CO_2).$$

490. DISTILLATION. Metallic zinc of commerce is purified by distillation. This process is conducted in a closed earthen crucible, A, *fig.* 136, immersed in a furnace. A tube, *a b*, conducts the vapour through a hole in the bottom to a pan C, placed below it.

TIN.

491. The ores of this metal, which are its oxide, occur in Cornwall, Saxony, Sweden, and in the East. They are reduced by charcoal or pitcoal.

It is one of the metals most anciently known. It has a whiteness nearly equal to that of silver, with, however, a yellowish tint. It exhales a peculiar and disagreeable odour when rubbed with the hand, is very malleable, and may be reduced under the hammer to thin leaves. It has but little tenacity, a wire a line in diameter being broken by a weight of 50 lb.

492. When a plate or slip of the metal is bent, it produces a peculiar crackling noise, called the *creaking or cry of tin*. It is one of the softest and least elastic of the metals, and consequently has little sonorousness. Its SG = 7·285, and is but little augmented by hammering. It fuses at 450°, and does not volatilise at the highest temperatures. It has a great tendency to crystallise, sometimes in the regular, and sometimes in the pyramidal system. Its crystalline texture is rendered manifest by the application of an acid.

493. If the metal, fused at the lowest possible temperature, be constantly agitated with a brush until it cools, it will be obtained in a powder, which, mixed with melted glue, is used for metallic paint.

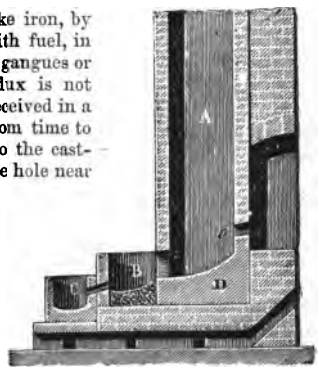
494. At common temperatures it is not oxidated, even in humid air, and may therefore be exposed without tarnishing. When heated, it oxidises rapidly. It decomposes water at a red heat, being converted into stannic acid, SnO_2, HO.

Sulphuric acid, when diluted, has no effect upon it; but when concentrated and boiling, oxidises it rapidly. Hydrochloric acid dissolves it, disengaging hydrogen—

$$Sn + HCl = SnCl + H.$$

Weak nitric acid acts slowly upon it. Aqua regia dissolves it rapidly. The hydrated alkalies act upon it, disengaging hydrogen. It combines directly with sulphur, phosphorus, arsenic, chlorine, and a great number of the metals.

Fig. 137.



495. EXTRACTION. Tin is extracted like iron, by depositing its ore in layers alternately with fuel, in tall blast furnaces, A, *figs.* 137, 138. The gangues or impurities being themselves fusible, a flux is not necessary. The impure fused metal is received in a basin B, and the scoriæ being removed from time to time, the pure metal is allowed to flow into the cast-iron pot C, by removing the plug from the hole near the bottom of B.

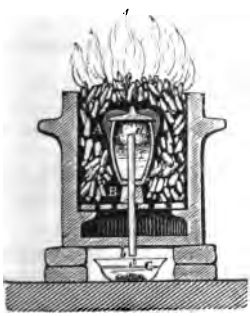


Fig. 136.

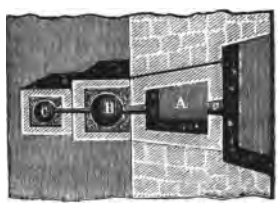


Fig. 138.

496. THE OXIDES are variously enumerated and named by different chemical authorities. The most important of them is the protoxide SnO, and the binoxide SnO_2, called by some the peroxide, and by others *stannic acid.* A sesquioxide, Sn_2O_3, also exists.

497. THE PROTOXIDE, SnO, may be obtained in the state of a

hydrate, SnO, HO, by heating the protochloride, SnCl, with carbonate of potash—

$$SnCl + KO,CO_2,HO = SnO,HO + KCl + CO_2.$$

It is white, insoluble in water, and when heated out of contact with air, it parts with its water, and is reduced to the anhydrous oxide, SnO.

This oxide plays the part of an acid, combining with bases to form *stannites*, but it loses its solubility in alkalies when it becomes anhydrous.

The anhydrous oxide is insoluble in water, and in dilute alkaline solutions. It is easily dissolved in the acids. Heated in contact with air, it inflames like amadou, and is transformed into the binoxide.

498. THE BINOXIDE OR PEROXIDE, SnO_2, can be obtained in two isomeric states, which are clearly distinguishable by their chemical properties. The first, to which the name *metastannic acid* has been given, is a white powder, obtained by treating metallic tin with nitric acid. The second, called *stannic acid*, is prepared by decomposing the perchloride $SnCl_2$ by water.

499. METASTANNIC ACID is found native in crystals, in some of the ancient formations. The hydrate which results from the reaction of nitric acid, is $SnO_2, 2HO$, which at 212° becomes SnO_2, HO, and at a higher temperature is anhydrous. It is not decomposed by heat alone, but is decomposed by contact with carbon, and the combustible gases. It forms crystallised salts with the alkalies. It appears from some of its compounds, that its composition is more properly $Sn_5 O_{10}, 10HO$.

500. STANNIC ACID is a white gelatinous substance, insoluble in water, but easily dissolved in dilute nitric or sulphuric acid. When dried in a vacuum, its composition is SnO_2,HO. A slight elevation of temperature converts it into metastannic acid, without dismissing any of its water. It is easily dissolved in alkaline solutions.

501. SALTS. There are few salts of the protoxide. The sulphate, SnO,SO_3, is obtained by saturating dilute sulphuric acid when hot, with the hydrate of the protoxide. The nitrate is obtained by dissolving the hydrate of the protoxide in dilute nitric acid.

Metastannic acid enters into combination with the concentrated acids, and stannic acid is dissolved, even in the dilute acids. Salts are thus formed, of which these compounds are bases, but of these but little is yet known.

502. THE PROTOCHLORIDE, SnCl, may be obtained by heating metallic tin in a current of hydrochloric acid gas, when hydrogen is liberated—

$$Sn + HCl = SnCl + H.$$

This substance when anhydrous is brilliant, with a vitreous fracture. It is volatile, and distils at a white heat. It can be crystallised in large octohedrons. It has a styptic taste, is very soluble in water, its solution producing a considerable cold. It has a great tendency to absorb oxygen and chlorine. It effects the complete

reduction of many metallic oxides, as those of antimony, zinc, mercury, and silver. It reduces others to a lower state of oxidation, such as those of copper, iron, manganese, tungsten, and molybdenum. It forms double chlorides with the alkaline chlorides.

503. USES. It is known in commerce as the *salt of tin*, and is used in the preparation of the *purple of Cassius*. It is also largely used in dyeing, as a mordant and as a strong deoxidant, and to produce white figures on grounds coloured by the peroxide of iron, and upon bistre grounds coloured by the peroxide of manganese. It also enters into the composition of the blues and greens employed in the "topical style" of calico-printing.

504. THE PERCHLORIDE, $SnCl_2$, is prepared by heating the protochloride in an excess of dry chlorine gas. When anhydrous it is a colourless liquid, which diffuses white fumes, combining with the water contained in the air. It has been hence called the *fuming liquor of Libavius*, who discovered it. Its SG = 2·28. It can be distilled without decomposition. It boils at 248°. Its vapour has SG = 9·2.

It has a great affinity for water, with which it combines, disengaging heat, and forming a crystalline hydrate, $SnCl_2, 5HO$. It is decomposed by alcohol. It combines with chlorine, sulphur, ammonia, and a great number of the metallic chlorides.

505. USES. It is employed in preparing stuffs to receive steam colours, and in making the colours used in the topical style of calico-printing. It is known in commerce as the *oxy-muriate of tin*.

506. THE SULPHURETS of tin are SnS, Sn_2S_3, and SnS_2, and therefore correspond in composition with the oxides. The most important is the last.

507. THE PERSULPHURET, SnS_2, is obtained in the humid way, by heating a solution of the perchloride by hydrosulphuric acid. Thus obtained it is a dirty yellow substance, insoluble in water and soluble in potash, from which it is precipitated by the acids.

By the dry way the process consists in raising to a low red heat, in a retort, a mixture of 2 parts of the peroxide, 2 of sulphur, and 1 of sal ammoniac. The sulphide remains in the form of golden yellow scales, with a metallic lustre.

This compound is commonly known as *mosaic gold*. It is not attacked by the acids, except aqua regia.

508. USES OF TIN. This, being a metal which resists most of the common reagents, is employed in many vessels and utensils for domestic use. It is also used to coat the interior of copper culinary vessels, which are then said to be *tinned*. Great quantities are used in the state of tinfoil, for preserving various substances from the action of air and moisture, and in silvering mirrors. The metal is also used in the fabrication of bronze, and in making plumbers' solder. As already stated, the chlorides are used as mordants in dyeing, and calico-printing. The metal is also used in the production of the purple of Cassius, mosaic gold, mineral lake, and various other substances.

One of the most extensive applications of the metal is in the manufacture of *tin-plate*, the material of which all so-called *tin* vessels and utensils are formed. Tin-plate is thin sheet iron, coated with tin.

ANTIMONY.

509. Antimony is a solid metal of the colour of zinc, brittle and easily pulverised. It is of lamellous crystalline structure, its primitive form being the octohedron. Its SG = 6·702. It fuses at about 800°, and volatilises at a red heat, but cannot be distilled like zinc in stoneware retorts. It remains unaltered at common temperatures in air and water; but when raised in air to its point of fusion, it oxidises. Nitric acid even when diluted attacks it, converting it into the antimoniate of the protoxide. It differs from most of the metals, tin excepted, in thus being attacked by nitric acid without being dissolved.

The other acids diluted have no action on it. Sulphuric acid concentrated and hot, attacks it, forming sulphate of antimony, and disengaging sulphurous acid. Hydrochloric acid acts but feebly upon it. Its usual solvent is aqua regia.

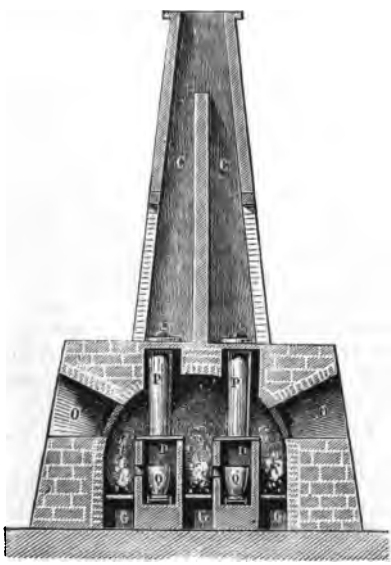


Fig. 139.

510. EXTRACTION. The ore which supplies it is its sulphuret, which is first separated from its impurities by fusion in a series of crucibles P P, *fig.* 139, disposed in a furnace having holes in the bottom, through which the fused ore descends into earthen pots Q. The purified ore thus obtained, is called *raw antimony*. This after being roasted in a common reverberating furnace, is mixed with about 15 per cent. of charcoal, and raised to a red heat in crucibles, in the bottom of which the metal subsides, the scoriæ floating upon it. These scoriæ sometimes called *crocus*, are employed in veterinary medicine. The metallic antimony is known by the name *regulus of antimony*, given it by the alchemists, who regarded it as a royal metal.

511. USES. This metal and its compounds are used chiefly in medicine, and in making the alloys called type metal, stereotype metal, music plates, and Britannia metal.

512. OXIDES. Chemists are not agreed as to the equivalent of antimony. According to the English authorities, it is 120·3, and according to the French 60·1. This produces a difference in the formulæ, for in its compounds Sb in the English corresponds to Sb_2 in the French. Adopting the English equivalent, the compounds with oxygen are the oxide, SbO_3, and antimonic acid, SbO_5. According to some authorities, there is an intermediate compound, SbO_4, called *antimonious acid*, which, however, others regard as a compound of the oxide and acid SbO_3, $SbO_5 = 2(SbO_4)$.

513. THE OXIDE, SbO_3, is obtained by various processes, one of which consists in calcining antimony in contact with air. The oxide is then produced in crystalline needles, called the *argentine flowers of antimony.*

This oxide is pearly white when anhydrous. Its SG = 5·56. It fuses at a red heat, and volatilises at a higher temperature. It is not decomposable by heat alone. It is reduced by charcoal and hydrogen at a high temperature.

When hydrated it is SbO_3, HO. In this state it is easily dissolved in the alkalies, even when diluted, and forms with them salts called *antimonites*, which however are very instable, being decomposed by mere evaporation.

This oxide is found native in Bohemia, in the form of brilliant white crystals.

514. ANTIMONIC ACID, SbO_5, when anhydrous, is pale yellow, its hydrate being white. It is slightly soluble in water, but rendered insoluble by the presence of a strong acid, such as nitric or hydrochloric acid. When hydrated this acid reddens litmus, and is dissolved slowly in the cold, in potash and ammonia; under the influence of heat its dissolution is very rapid.

In the hydrated state, it is obtained by several methods, one of which is to treat antimony with aqua regia, containing an excess of nitric acid; and another to act upon the perchloride with water—

$$SbCl_5 + 5HO = SbO_5 + 5HCl.$$

The acid obtained by this process is called meta-antimonic acid, the name antimonic acid being limited to the acid obtained by the first-mentioned process.

515. THE PROTOCHLORIDE, $SbCl_3$, formerly known as *butter of antimony*, in its anhydrous state is crystallised in colourless octohedrons, which are fusible and volatile at a moderate temperature. Its vapour has SG = 8·10. It is deliquescent, soluble without decomposition in a small proportion of water, and especially in an acid liquor; but when the solution is diluted with water, it is decomposed, giving hydrochloric acid, and an insoluble oxychloride, formerly called the *powder of algaroth*, the composition of which is $SbCl_3$, $2(SbO_3)$, HO.

It combines with hydrochloric acid, producing an hydrochlorate of the chloride, formerly called the *liquid butter of antimony.*

516. PREPARATION. The chloride is obtained by several methods, one of which is the distillation of 1 part of antimony, with 2 of chloride of mercury.

517. USES. In medicine as a caustic. It is used to cauterise the bites of

mad dogs. Gunsmiths use it to bronze gun barrels, on the surface of which it forms a brown coat of metallic antimony, which preserves the iron from further oxidation.

518. THE PERCHLORIDE, $SbCl_5$, corresponds to antimonic acid. It is colourless or slightly yellow, liquid, and very volatile. It diffuses in air suffocating white fumes. Water converts it, first, into a crystalline hydrate, and then resolves it into hydrochloric and antimonic acids—

$$SbCl_5 + 4HO = SbO_5 + 5HCl.$$

519. PREPARATION,—by heating antimony in small fragments in a current of dry chlorine in excess. The process is conducted in an apparatus such as that shown in *fig.* 112.

520. THE SULPHURETS correspond in composition to the oxides, and are SbS_3 and SbS_5. According to some chemists there is a third, SbS.

521. THE PROTOSULPHURET or TERSULPHURET, SbS_3, is the common ore of the metal. It has a bluish gray colour, a strong metallic lustre, is lamellous, fragile, and tender. It crystallises in tetrahedral prisms or needles. Its SG = 4·62. Its matrix is usually quartz, sulphate of baryta, and iron pyrites. It is very fusible, being easily liquified at the flame of a candle. It is volatile, and may be distilled in a current of nitrogen or carbonic acid. It is easily roasted, and transformed into the oxide and oxysulphuret. Carbon decomposes it at a white heat. It is also decomposed by iron, copper, and several other metals. It is readily attacked by acids. Concentrated hydrochloric acid dissolves it at a feeble heat, producing sulphuretted hydrogen. The alkalies and alkaline carbonates also decompose it—

$$SbS_3 + 4KO = KO,SO_3 + 3KS.$$

Nitre attacks it at a dull red heat.

522. THE OXYSULPHURET OR KERMES, $2SbS_3 + SbO_3$, is found native, and known as *red antimony*. It has a brownish yellow colour, and is much used in medicine on the Continent. In this country the protosulphuret is preferred.

ARSENIC.

523. Arsenic is a solid, of an iron gray colour, with metallic lustre. It is very brittle: at a red heat it sublimes without fusion;—under pressure, however, fusion precedes evaporation. Its vapour is colourless, has an alliaceous odour, with SG = 10·37. The SG of the metal = 5·75.

It is combustible, and burns with a livid flame, producing arsenious acid, which is the common *arsenic* of the shops.

Metallic arsenic is not itself poisonous. It is only rendered so by combination with oxygen.

524. The compounds of arsenic with oxygen are AsO_3, and AsO_5, similar to those of phosphorus, with which this metal has a close analogy.

525. ARSENIOUS ACID, AsO_3, commonly called *arsenic*, is produced by heating metallic arsenic in oxygen. It is an extensive article of commerce, being consumed in large quantities in painting, combined with copper, forming a fine green paint. It is only a feeble acid, its solution faintly reddening litmus paper. At common temperatures it has no sensible odour. Thrown on burning charcoal it emits a strong odour of garlic.

526. PHYSIOLOGICAL EFFECTS. Taken in minute doses—half a grain, for example, every other day,—it is found to stimulate the development of fat, and thereby to give plumpness to the figure, smoothness and softness to the skin, and beauty and freshness to the complexion. It has also a specific action on respiration, giving to that function augmented efficiency, so as to enable the recipient to undergo extraordinary bodily exertion, such as running and mounting hills without being put out of breath. Its use for these purposes has been general by both sexes for ages, in certain parts of Germany, where it has also been administered with similar results to the lower animals, such as horses and other beasts of burden. Like other stimulants, however, its discontinuance after long-continued use is attended with the extreme opposite effects. Its mode of action on the animal body, in the production of these effects, has not been explained, but the facts appear to be undisputed.*

527. POISONING. Taken in larger doses it is an irritant poison, by which it appears from statistical reports, that a greater number of lives have been destroyed than by all other poisonous drugs taken together. This circumstance, and its frequent use of late years as an instrument of homicide, renders it not inappropriate even in a volume so elementary as the present, to explain in a summary manner, the antidotes which may be resorted to, in cases where fatal effects have not yet ensued, and the means of detection where all remedies are too late.

528. ANTIDOTES. If the poison has continued in the stomach and intestines long enough to have passed by absorption into the circulation, no antidote can counteract it. But if not, emetics should first be administered to cause the ejection of as much of the poison as possible. Whatever may still remain, should then be rendered innoxious by the administration of some substance which will enter into combination with arsenious acid, so as to produce an insoluble and therefore an unabsorbable compound. The hydrate of the peroxide of iron, $Fe_2O_3,3HO$, and caustic magnesia, MgO, have each that property, and especially the latter. The one produces with arsenious acid the arsenite of iron, which is insoluble; and the other, the arsenite of magnesia, also insoluble. These would pass off through the intestines without entering the circulation, and therefore without injury.

529. DETECTION. In cases in which poisoning by arsenic is suspected, the poison may be sought for either in a part of the food with which it has been mixed, if any can be found, or in the matter brought from the stomach by emetics, or in that discharged from the bowels, in the stools and in the urine. In *post mortem* investigations it must be sought for on the coats of the stomach and intestinal canal, and if time has been allowed for absorption, in various organs, and more especially in the liver.

* See Johnston's Chemistry of Common Life, ii. 202.

Various processes for the detection of the poison have been proposed by Rapp, Orfila, Duvergier, Flandin, Danger, and others. It will be sufficient here to notice that of Dr. Marsh.

530. MARSH'S PROCESS is based upon the property by which arsenic leaves its compounds to combine with nascent hydrogen. The arseniuretted hydrogen thus obtained, being decomposed by heat, gives the metallic arsenic either pure, or combined with oxygen as arsenious acid.

The form of apparatus for this process is shown in *fig.* 140. The hydrogen is developed in the flask A, by the process explained in § 86. The suspected arsenic is introduced through the tube *n m*, and, assuming its presence, it combines with the nascent hydrogen, and issues with aqueous vapour through the rectangular tube *a b*. The vapour is condensed in the bulb, and the

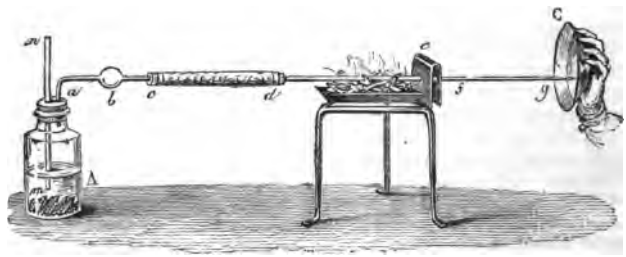


Fig. 140.

arseniuretted gas passes through the tube *e d*, which is filled with amianthus or cotton, by which any portion of the sulphate of zinc formed in A, which may come over, shall be intercepted. The gas is decomposed in the tube *d e* by heat, and after a certain time, the metallic arsenic resulting from such decomposition will be deposited in the tube *f g*. A metallic screen is placed at *e*, to prevent the transmission of heat from the fire to the tube *f g*, in which the metallic arsenic is condensed.

If the decomposition of the arseniuret be not complete (which it rarely is), the flame of the undecomposed gas received at *g* upon a porcelain saucer, C, will produce arsenical mirrors upon it.

531. ARSENIC ACID, AsO_5, may be obtained by boiling a solution of arsenious acid in aqua regia. The liquor being evaporated until the hydrochloric and nitric acids are expelled, and the residuum dried, dissolved in water, and evaporated, crystallised arsenic acid is obtained.

532. ARSENIURETTED HYDROGEN, AsH_3, already mentioned, is a colourless gas, of a characteristic and nauseous alliaceous odour, with SG = 2·69. It is liquified at −22° under common pressure, and has not been solidified. It has no action on litmus. Water dissolves about 20 per cent of it. Heat resolves it, as already stated, into hydrogen and metallic arsenic.

533. Arsenic combines with chlorine, iodine, and bromine, forming the compounds $AsCl_3$, AsI_5, and $AsBr_3$, which do not require particular notice here.

534. THE SULPHURETS are AsS_2, AsS_3, and AsS_5. The bisulphuret AsS_2 is a red translucent solid, which may be sublimed in close vessels. It is known in mineralogy as *realgar*. The *tersulphuret* AsS_3, is an orange yellow solid, which is fusible, and may be sublimed in close vessels. It is known in mineralogy as *orpiment*, and is an ingredient of *king's yellow*. It is used in dyeing. The *persulphuret*, AsS_5, is of a paler yellow, is soluble in alkalies, is fusible, and volatilises without change. This compound is also called *sulph-arsenic acid*.

CHAPTER XVI.

BISMUTH.—LEAD.—COPPER.

BISMUTH.

535. BISMUTH is a grayish white metal with a slight reddish tint, SG = 9·9, and a crystalline brittle structure. It fuses at about 500°, volatilising at a much higher temperature. At common temperatures it is but little oxidised in the air; but when strongly heated, burns with a bluish flame. Nitric acid, a little diluted, freely dissolves it.

Chemists differ as to its equivalent. According to most English authorities Bi = 213. Regnault and other French chemists assign to it the half of this, and Dr. Gregory gives it one-third of it. This difference causes an apparent discrepancy in the constitution assigned by different authorities to its compounds. We shall here follow the common English estimate, Bi = 213.

536. OXIDES. It forms with oxygen two principal combinations, the teroxide, BiO_3, and the peroxide, or bismuthic acid, BiO_5.

537. THE TEROXIDE, the base of all the salts of bismuth, is a straw-yellow powder, prepared by gently igniting the neutral or basic nitrate. It is fusible at a high temperature, and when fused, acts as a powerful flux on silicious compounds.

The hydrate of the teroxide, BiO_3, HO, is obtained by precipitating a salt of bismuth by potash or ammonia in slight excess.

The anhydrous oxide is yellow, fixed, and without odour or taste. It is fused at a red heat, traverses the crucible like litharge, and is easily decomposed by carbon, hydrogen, sulphur, or chlorine.

538. BISMUTHIC ACID, BiO_5, as yet but little known, is prepared, according to Arppe, by transmitting a current of chlorine gas through a very concentrated solution of potash, holding in suspension the oxide of bismuth. Jacquelain obtained the bismuthate of potash by calcining in air a mixture of potash and the oxide of bismuth.

539. THE SALTS OF BISMUTH have all an acid reaction, are decomposed by water into subsalts, which are precipitated, and acid salts which remain in solution. An excess of acid prevents this decomposition. They are almost all colourless and give with potash, ammonia, their carbonates, and ferrocyanide of

potassium, a white precipitate; with ferridcyanide of potassium, tannin, and chromate of potash, a yellow precipitate; and with hydrosulphuric acid and hydrosulphate of ammonia, a black precipitate.

Zinc precipitates bismuth from its solutions in the form of a black spongy mass. Copper and tin also precipitate it in the metallic state.

540. THE ALLOYS of bismuth are remarkable for their fusibility, a property known so early as the time of Newton, whose name has been given to an alloy which melts below the heat of boiling-water, consisting of 8 parts of bismuth, 5 of lead, and 3 of tin. Another, called Arcet's fusible metal, which melts at a somewhat lower temperature, consists of 2 parts of bismuth, 1 of lead, and 1 of tin.

541. THE METALLURGY OF BISMUTH presents no difficulty, the metal being almost always found native. When not so, it is generally sufficient to raise the ore to a red heat in crucibles, when the metal is reduced and deposited on fusion.

LEAD.

542. LEAD, Pb, is a metal of a blackish gray colour, the surface of which becomes tarnished when exposed to the air, but has a strong metallic lustre when freshly cut. It is so soft that sheets of considerable thickness can be easily bent. It can be scratched with the nail, and when rubbed on paper, leaves traces of a gray colour. When pure its SG = 11·445, but for the lead of commerce SG = 11·352. The density, instead of being increased under the hammer, is slightly diminished. Its malleability is relatively greater than its ductility. It can be reduced to thin and flexible wires, which, however, have but little tenacity; a wire of a line in diameter being broken by a weight of 181b. to 201b. Its point of fusion is 633°. At a more elevated temperature it is sensibly volatilised, and diffuses visible fumes. It has the property of dissolving its own oxide, which imparts to it a certain degree of hardness; a circumstance which may explain the modifications which the metal undergoes in some of its physical properties when it has been kept a long time in fusion in contact with air. To restore it to its proper softness it is necessary to stir it while in a state of fusion, with a little carbon, which reduces the oxide.

Lead slowly cooled, crystallises in 4-sided prisms, and regular octohedrons. Exposed to humid air, it is covered with a gray coating of oxide, which preserves the remainder of the metal from oxidation.

In distilled water in contact with air, it is soon oxidised. Dilute sulphuric and hydrochloric acids attack it with much difficulty. Concentrated sulphuric acid dissolves it when hot, forming sulphurous acid and sulphate of lead. The best solvent for lead, however, is nitric acid.

543. THE OXIDES are : 1°. the suboxide, Pb_2O ; 2°. the protoxide, PbO ; 3°. the peroxide, PbO_2. Other oxygenised compounds, called *miniums*, are produced by the combination of these.

544. THE SUBOXIDE, Pb_2O, according to Dulong, may be obtained by heating the oxalate PbO,C_2O_3 at 570°, until gas ceases to be disengaged from it—

$$2(PbO,C_2O_3) = Pb_2O + 3CO_2 + CO.$$

The black coating which collects on fused lead exposed to moist air, is said to be this oxide. It existence is, however, not generally admitted, and has been rendered questionable by the experiments of Boussingault and Pelouze.

545. THE PROTOXIDE, PbO, when prepared by the dry way without fusion, is the *massicot* of commerce. When it has been fused, it becomes *litharge*.

It is a solid, the colour of which varies from lemon to reddish yellow. It is fusible below a red heat, and in cooling crystallises in micaceous plates.

When litharge is fused in an earthern crucible, it combines with the silica of the vessel, forming a fusible silicate, so that the crucible is soon destroyed.

The protoxide is sensibly soluble in pure water, which it renders alkaline ; one part is dissolved by 7000 parts of water. It is not soluble in water which holds a salt in solution.

Since it combines with all the acids, including even carbonic acid, it may be considered as a strong base, analogous to the alkaline earths. Heated in air, it absorbs oxygen, and is converted into the sesquioxide—

$$2(PbO) + O = Pb_2O_3.$$

This compound is regarded by some chemists as the plumbate of the protoxide PbO, PbO_2, the peroxide being considered as playing the part of an acid, in relation to the protoxide as a base.

The protoxide is easily reduced by hydrogen—

$$PbO + H = Pb + HO,$$

or by carbon—

$$2(PbO) + C = 2Pb + CO_2,$$

water being produced in the one reaction, and carbonic acid or carbonic oxide in the other.

According to Leblanc, litharge fused in air absorbs oxygen, which it dismisses when cooled. Silver also has this curious property.

546. The protoxide plays the part of a base with acids, and of an acid with strong bases, forming salts called *Plumbites*.

The plumbites of potash and soda are soluble in water. That of lime, obtained by boiling the oxide with milk of lime, may be crystallised. This

compound is used as a black dye for the hair. The lead combines with the sulphur contained in the hair to form a black sulphuret.

547. THE PEROXIDE PbO_2, or puce-coloured oxide, is considered to be entitled to the name of an acid, since it combines with the metallic bases to form a series of saline compounds. It is therefore called by some chemists *Plumbic acid*, these salts being called *plumbates*, and being expressed by the general formula MO, PbO_2.

This oxide is solid, has a rich brown colour approaching to black. It is decomposed below a red heat, being resolved first into minium, and then into litharge. It is reduced in contact with ammonia, producing water and nitrate of ammonia. Several organic substances decompose it in the presence of water, undergoing an imperfect combustion. Mixed with a sixth of its weight of sulphur, it forms a powder which ignites by friction. It absorbs sulphurous gas with great elevation of temperature—

$$PbO_2 + SO_2 = PbO, SO_3,$$

producing sulphate of lead.

548. MINIUMS are compounds in different proportions of the protoxide and plumbic acid. The varieties consist of a single equivalent of plumbic acid combined with 1, 2, 3, and 5 of the protoxide. The composition of the most common sort is $2(PbO), PbO_2$.

These compounds present all the chemical characters of *plumbates*. Thus they are decomposed by the acids which combine with the protoxide, plumbic acid being precipitated.

Minium may be prepared by heating the pulverised protoxide, or massicot, in air at a regulated temperature, when it will absorb oxygen, and be converted into a fine orange-red powder. If the process be continued until the absorption of oxygen has attained its limit, the compound resulting will be $2(PbO), PbO_2$, the most ordinary composition of minium.

This compound is largely used in the manufacture of flint-glass. It is the substance commonly known as *red lead*.

549. THE SALTS OF LEAD have the protoxide as their base. They are poisonous, and in minute doses produce bowel pains and colic. House painters are subject to a malady of the intestines which they call *lead colic*. The remedy found most efficacious is a drink containing a small proportion of sulphuric acid, or sulphate of soda, in order to carry off the sulphate of lead as an insoluble sulphate.

550. SULPHURET OF LEAD, PbS, called *galena*, is the most common ore, and almost the only one from which the metal is extracted. It is a bluish-gray mineral, of strong metallic lustre. It is fragile, and crystallises in cubes. Its SG = 7.585. It is less fusible than lead, and cannot be maintained in fusion in the crucibles because it passes through them. It is partly decomposed by heat, a part volatilising, and the remainder forming a sub-

sulphuret. Hydrogen deprives it of its sulphur under the influence of heat. The vapour of water decomposes it, producing sulphurous acid, sulphuretted hydrogen, free hydrogen, and metallic lead.

$$2(PbS) + 2HO = 2Pb + SO_2 + HS + H.$$

When roasted in contact with air it is transformed into oxide and sulphate of lead, disengaging sulphurous acid.

$$2(PbS) + 7O = PbO + PbO,SO_3 + SO_2.$$

Nitric acid converts it into sulphate of lead, disengaging nitrous oxide.

$$PbS + NO_5 = PbO,SO_3 + NO.$$

Hydrochloric acid acts upon it only after a long interval, producing chloride of lead, and disengaging sulphuretted hydrogen.

$$PbS + HCl = PbCl + HS.$$

The other acids are without action upon it.

551. GALENA, or the native sulphuret, is found in veins, and sometimes in masses, in the primitive formations. It appears generally in layers in the intermediate formations, or in the first deposits of the secondary strata. Two varieties are known, the *lamellar* and *compact*.

552. THE NITRATE, PbO, NO_5, may be obtained by dissolving metallic lead, the oxide, or the carbonate, in nitric acid. This salt crystallises in regular octohedrons, which are sometimes opaque and sometimes transparent, but always anhydrous. It is insoluble in alcohol, but soluble in seven times its own weight of cold, and in a less proportion of boiling, water. It is decomposed by heat, disengaging oxygen and nitrous acid, and leaving a residuum of the protoxide of lead. In virtue of this property nitrate of lead is used in laboratories for the preparation of nitrous acid.

553. THE SULPHATE, PbO, SO_3, is white pulverulent crystalline, insipid, anhydrous, and almost insoluble in water, but soluble in the acids. Hydrochloric acid decomposes it, producing free sulphuric acid and the chloride of lead.

$$PbO,SO_3 + HCl = PbCl + SO_3 + HO.$$

Heated in a solution of carbonate of soda double decomposition takes place, and the carbonate of lead and sulphate of soda are produced. The same reaction is produced by the dry way.

$$PbO,SO_3 + NaO,CO_2 = PbO,CO_2 + NaO,SO_3.$$

554. THE CARBONATE, PbO,CO_2, is a white pulverulent substance, insoluble in water, sensibly soluble in carbonic acid, decomposed by heat, disengaging carbonic acid, and leaving the oxide PbO. Heated in contact with air, at a temperature below the point of fusion of the protoxide, it is converted into the substance

called *orange minium*, of a brilliant colour, lighter than that of common minium. This operationis usually performed by slowly calcining the best quality of the carbonate in iron trays.

555. The carbonate is the well-known pigment *white lead*. As a paint, mixed with drying oils, such as linseed, it forms the base of all the oil paints. Bruised up with a small quantity of oil it constitutes putty; but in general the glazers substitute chalk for it. A mixture of equal parts of white lead, minium, and linseed oil, forms a putty which becomes as hard as stone.

556. THE SILICATE OF LEAD enters into the composition of glass and the glazes of earthenware. It melts at a comparatively low temperature, its fusibility being increased with the proportion of the oxide of lead which it contains. When the silicic acid is in excess the silicate is colourless; but when the oxide predominates it is yellow, or yellowish brown.

557. THE CHROMATE, PbO, CrO_3, commonly known as *chrome yellow*, is insoluble in water, sparingly soluble in the acids, and easily reduced by carbon and organic substances. It may be obtained by double decomposition by precipitating neutral chromate of potash KO, CrO_3 by the neutral acetate $PbO, C_4H_3O_3$.

$$KO,CrO_3 + PbO,C_4H_3O_3 = PbO,CrO_3 + KO,C_4H_3O_3.$$

The colour of the precipitate will vary with the state of neutrality of the salts employed, and even with the temperature at which the precipitation takes place. It is necessary to operate with very dilute liquors, to avoid the production of a silky compound, which is probably a double salt.

558. The chromate of potash gives with the basic salts of lead precipitates, which are so much the more red as they contain a greater quantity of the oxide of lead.

USES. The chromate of lead is employed largely in oil-painting and in calico printing, to produce a yellow colour. It is used in laboratories for the analysis of certain sulphuretted organic compounds. It gives up its oxygen to these substances, water, carbonic acid, and the sulphate of lead, being formed. The chromate of lead of commerce is often mixed with a certain quantity of the sulphate of lime, which seems to heighten its lustre.

The compound known under the name of *Cologne yellow* contains 25 parts of the chromate, 15 of the sulphate of lead, and 60 of the sulphate of lime.

559. The chromate of lead is found native, and it was in analysing this mineral that Vauquelin discovered chromium. The native chromate of lead, called *red-lead ore*, is found chiefly in Siberia. It has a fine orange-red colour, being, however, yellow when pulverised. It crystallises in oblique, yellow, rhomboidal prisms.

560. ALLOYS OF LEAD. Lead may be alloyed with almost all the metals; but we shall here notice only those combinations which are useful in the arts.

It forms with tin different alloys less brilliant than tin, but harder and more fusible. The alloy composed of equal parts of tin and lead forms *plumbers' solder*. This alloy is more oxidable than either of its constituents. It is also used to produce the stannate of lead, which enters into the composition of the glaze of pottery.

561. Tin and its alloys with lead may be thus classed, in relation to their uses in the arts.

1°. Pure tin is employed in culinary utensils.
2°. An alloy of 8 parts of lead and 92 of tin is used as *pewter*.
3°. An alloy of 20 of lead with 80 of tin is used to make saucepans, candlesticks, &c.
4°. An alloy of 4 parts of lead and 1 of antimony constitutes *type metal*.

COPPER.

562. Copper, from its universal application to the uses of life, is familiar to every eye. It has a characteristic reddish-brown colour, and strong metallic lustre. In malleability it is inferior only to gold and silver, being reduced under the hammer to leaves of a tenuity so great as to be partially translucent, the light they transmit being greenish, a colour complementary to that which is reflected by the metal. In ductility copper stands next to iron, being reduced by the draw-plate to fine threads. In tenacity it is only inferior to iron, a wire of a line diameter supporting by suspension $2\frac{1}{2}$ cwt. As a conductor of heat it holds a rank next to gold, silver, and platinum, and holds the first place as a conductor of electricity. The SG of fused copper is 8·780; that of wire-drawn, 8·96. It is fused at a red heat, and at a white heat is sensibly vaporised, the vapour producing a green flame when ignited. Nevertheless, it appears from the experiments of Berthier that it is scarcely volatile. That chemist maintained that metal for a long interval at the temperature of a porcelain oven, and ascertained that it had not lost more than one-half per cent of its weight.

563. Copper has but a feeble affinity for oxygen. In air, and even in pure oxygen, when dry, it is not attacked at common temperatures. In moist air, especially if acid vapours be present, it is soon coated with an oxidised matter called *verdigris* (*vert-digris*), which is an hydrocarbonate of the metal. If it be raised to a high temperature oxidation takes place; a coating of the red oxide (Cu_2O) collects on it, and this after a time is further oxidised and converted into the black oxide (CuO).

It decomposes water very slowly, and only at a very high temperature. No decomposition takes place at common temperatures, even in the presence of the strongest acids.

Nitric acid, even when diluted and cold, readily attacks it, producing the nitrate of the black oxide (CuO,NO_5) and the black oxide CuO.

564. Sulphuric acid when dilute has no action on it, but if it be concentrated it acts at a high temperature, producing the sulphate, CuO,SO_3, and sulphurous acid, SO_2.

Hydrochloric acid attacks it with difficulty, and only when in a state of subdivision, producing the protochloride—

$$HCl + 2Cu = H + Cu_2Cl.$$

Aqua regia rapidly dissolves it. Its oxidation is also easily produced by organic matters, the fats and fat oils. It is therefore an unfit material for culinary vessels, unless it be coated with a less oxidable metal. Copper vessels for domestic purposes are therefore *tinned* on their inner surfaces.

Ammonia dissolves copper under the influence of the oxygen of the air, forming the black oxide, CuO, which being dissolved by the ammonia produces a blue solution.

Nitre may be fused in a copper vessel without attacking the metal in a sensible degree. It is oxidised, however, if the vessel be raised to a red heat.

Copper is rapidly dissolved by a weak solution of common salt, while a concentrated solution does not sensibly affect it: hence the copper sheathing of ships is soon corroded.

Sulphur, phosphorus, arsenic, chlorine, bromine, and most of the metals, combine directly with copper, the combination being sometimes attended with a development of heat, and even of light. A small proportion of phosphorus and arsenic combining with copper renders it white, hard, and brittle. Carbon does not combine with it in definite proportions. A known weight of copper kept for an indefinite time in fusion in a brasque crucible acquires no sensible increase of weight.

565. If copper be fused in any considerable quantity in a crucible, and after slow cooling the part still liquid be poured off, the solid part will be found crystallised in regular octohedrons. The metal when found native is often crystallised in this form. When crystallised by slow precipitation by the voltaic current, crystals of the same form, or that of the cube of which the octohedron is a derivative, are obtained.

566. Copper chemically pure may be obtained by transmitting a current of hydrogen through its oxide contained in a heated tube. This reduction is effected at a red heat, and the metal remains as a reddish powder, which when submitted to the burnisher acquires a fine metallic lustre.

567. THE OXIDES are four, the composition of three only being known—Cu_2O, CuO, and CuO_2. In the nomenclature of these much confusion prevails, owing to the different names given to the same compound. Thus, Cu_2O is called by different chemists the *red oxide*, the *suboxide*, the *protoxide*, and the *binoxide*. In the same way, CuO is called the *black oxide*, the *protoxide*, and the *deutoxide*. The compound CuO_2 is called the *deutoxide*, the *binoxide*, and the *peroxide*. The fourth, the composition of which is unascertained, is called *cupric acid*. We shall here, for clearness, call the three first severally the *red*, *black*, and *per-oxides*.

568. THE RED OXIDE, Cu_2O, when anhydrous, has a rose-red colour (from which it derives its name), and sometimes a vitreous lustre. It is occasionally found native in fine red crystals.

It may be obtained artificially by various processes, one of the most simple consisting of the fusion of one equivalent of metallic copper in an earthen crucible with one of the black oxide. Combination takes place, and the red oxide results.

$$CuO + Cu = Cu_2O.$$

It is obtained hydrated, $(Cu_2O)_4$, HO, by precipitating a solution of the protochloride, Cu_2Cl, by potash, when the hydrate is obtained as a blueish-gray precipitate.

$$4(Cu_2Cl) + 4KO + HO = (Cu_2O)_4.HO + 4(KCl).$$

This oxide is unalterable in air at common temperatures, but when heated is converted into the black oxide, CuO. It is highly unstable; it is decomposed by dilute acids, being resolved into metallic copper and the black oxide.

$$Cu_2O = CuO + Cu.$$

569. Nitric acid forms with it the nitrate of copper, disengaging ruddy vapours. It is dissolved by concentrated hydrochloric acid without being decomposed. It is soluble in ammonia. If the solution be kept out of contact with air it will be colourless, but the smallest addition of oxygen will render it blue, the red being changed into the black oxide. If a plate of copper be immersed in this blue solution the liquor will again become colourless, the black being reconverted into the red oxide, by taking one equivalent of copper from the metal.

$$CuO + Cu = Cu_2O.$$

570. Fused with fluxes, the red oxide produces a fine ruby-red glass, which if heated in contact with air becomes rapidly green, in consequence of the red being converted into the black oxide by absorbing oxygen.

$$Cu_2O + O = 2(CuO).$$

571. When found native this oxide is sometimes called the *oxidate*. It has generally a cochineal-red colour, but is occasionally gray, generally opaque, though sometimes translucent, and even transparent. Its crystals have the forms of the regular octohedron, and its derivatives. Its SG = 5·60. It is found at Chessy, in the department of the Rhône (France), and in the Altai Mountains.

572. The peroxide, CuO_2, is a brownish-yellow substance, obtained by sprinkling oxygenated water on the hydrate of the protoxide. It is very unstable, being decomposed by the heat of boiling water.

573. CUPRIC ACID. Copper in minute subdivision being well mixed up with potash and nitre, and after being raised to a red heat treated with water, gives a blue solution, which has been inferred to include an oxide of copper, more oxygenated than the black oxide, combined with potash. It is this hypothetic compound to which the name cupric acid has been given.

574. THE COMPOUNDS OF COPPER AND CHLORINE correspond to the oxides, being CuCl and Cu_2Cl.

575. THE PROTOCHLORIDE, CuCl, may be obtained by dissolving the black oxide, CuO, in hydrochloric acid, or by dissolving metallic copper in aqua regia.

$$CuO + HCl = CuCl + HO.$$

This chloride is very soluble in water. It crystallises when a concentrated solution is cooled, forming long needles of a greenish-blue colour, CuCl, 2HO.

576. THE SUBCHLORIDE, Cu_2Cl, may be obtained by boiling a solution of the protochloride, CuCl, with metallic copper in a minute state of subdivision. The liquor changes colour, being converted from green to brown, and a white crystalline powder is soon deposited, which is the subchloride.

$$CuCl + Cu = Cu_2Cl.$$

577. COMPOUNDS OF COPPER WITH SULPHUR. Copper burns brilliantly in the vapour of sulphur, and forms a subsulphuret,

Cu_2S, which corresponds to the red oxide and the subchloride. This sulphuret is fused more easily than metallic copper. It takes a crystalline texture in cooling.

Another sulphuret, CuS, analogous to the black oxide and protochloride, may be prepared by decomposing the solution of a salt of the black oxide by sulphuretted hydrogen.

578. THE SULPHATE, CuO, SO_3, the most important of the salts of copper, commonly known as *blue vitriol*, is a beautiful blue salt crystallising in oblique parallelopipeds with 5 equivalents of water, $CuO, SO_3, 5HO$. Its SG in this state is 2·19. It is soluble in four times its weight of cold, and twice its weight of boiling water, the solution being blue. In alcohol it is completely insoluble. In dry air it effloresces, losing 2 equivalents of water, and becoming opaque. At 212° it retains only a single equivalent of water, and when raised to 400° it is deprived of this last equivalent and rendered anhydrous, in the state of a nearly white powder, which put again in contact with water becomes hydrated and recovers its blue colour. At a still more elevated temperature the salt is completely decomposed, leaving the black oxide—

$$CuO, SO_3, = CuO + SO_2 + O.$$

579. The hydrated sulphate combines in all proportions with those of cobalt, nickel, and zinc. With the sulphate of iron it manifests some curious relations. If a solution of the sulphate of copper, $CuO, SO_3, 5HO$, be mixed with *an excess* of the sulphate of the protoxide of iron (green vitriol), $FeO, SO_3, 7HO$, and the liquor be evaporated and cooled, crystals of a double sulphate having the composition $(CuO, SO_3, 7HO)$ $(FeO, SO_3, 7HO)$ will be deposited, the copper sulphate taking up 2 additional equivalents of water to assimilate itself with the iron sulphate, the crystals being oblique parallelopipeds—a form common to both sulphates. But if, instead of the sulphate of iron, *that of copper be in excess*, the composition of the resulting double salt will be $(CuO, SO_3, 5HO)$ $(FeO, SO_3, 5HO)$, the hydration of the iron in that case assimilating itself to that proper to the copper.

580. The anhydrous sulphate absorbs dry ammoniacal gas, forming the compound $2(CuO, SO_3), NH_3$. Dissolved in liquid ammonia, it deposits crystals, leaving the composition $CuO, SO_3, (NH_3)_2, HO$. At 300° this compound is reduced to CuO, SO_3, NH_3, and at a more elevated temperature is completely decomposed, the residuum being the sulphates of the red and black oxides of copper.

581. PREPARATION. The sulphate may be prepared by various processes, one of the most simple of which consists in treating metallic copper with concentrated sulphuric acid.

$$2(SO_3,HO) + Cu = CuO,SO_3 + 2HO + SO_2.$$

582. USES. This salt is used in medicine as a slight escharotic. It has been also applied to destroy a peculiar fungus called *weeds*, developed in wheat. It is also used in the preparation of the insoluble salts of copper by double decomposition. It is applied in dyeing black, and in the manufacture of ink, and a considerable quantity is consumed in electro-metallurgy, in the smelting of silver ore in South America, and in the process of concentrating alcohol.

The chief part of the sulphate of copper of commerce is supplied by the works for refining silver.

583. THE NITRATE, $CuO,NO_5,4HO$ is a blue salt, which is deliquescent, very soluble in water, and soluble in alcohol. It is decomposed by heat, giving at first the basic nitrate $(CuO)_4$, NO_5. By a still higher temperature, the black oxide CuO is separated. Charcoal easily decomposes it, and sometimes with explosion.

This salt has a strong action on tin. If a piece of the nitrate be enveloped in tinfoil, and struck with a hammer upon an anvil, the tin will be oxidated with ignition, and transformed into stannic acid.

584. PREPARATION. This salt may be obtained by the reaction of nitric acid on metallic copper, nitric oxide being disengaged.

$$3Cu + 4NO_5 = 3(CuO,NO_5) + NO_2.$$

The liquor being evaporated deposits fine blue crystals, which include 4 and sometimes 6 equivalents of water. This salt has not been reduced to the anhydrous state.

585. THE SUB-NITRATE, $(CuO)_4$, NO_5, which, according to Gerhardt, always includes 3 equivalents of water, may be prepared by decomposing the nitrate by heat.

586. THE CARBONATES are two, distinguished as the *bibasic* $(CuO)_2$, CO_2, 2HO, and the *sesquibasic* $(CuO)_3$, $(CO_2)_2$, HO.

587. THE BIBASIC carbonate is obtained by precipitating cold a salt of copper by an alkaline carbonate, when it is deposited as a bluish bulky powder, which becomes green when the water which holds it in suspension is slightly heated, losing at the same time an equivalent of water. By continued boiling it parts with its carbonic acid, the anhydrous black oxide remaining.

$$(CuO)_2,CO_2, 2HO = 2(CuO) + CO_2 + 2HO.$$

This salt, when monohydrated, is used in oil painting, under the name of *mineral green.*

588. When native, it is the mineral known as *malachite.* Its SG = 2·5. It is hard, and susceptible of a fine polish. It is used for works of art, such as vases, statuettes, and the like. Malachite is found crystallised in right rhomboidal prisms, but more frequently in concentrical compact masses, having a silky fracture. The finest specimens of this mineral come from the Oural mountains.

589. THE SESQUIBASIC CARBONATE, remarkable for its fine dark blue colour, is found native, and is known as *mountain blue*, or *azurite.* When pulverised it is sky blue, and known as *blue ashes.*

590. ALLOYS. Copper forms alloys with almost all the other metals, and these compounds are extensively applied in the arts. The alloys of copper and

zinc especially, being cheaper than pure copper, and having physical and mechanical qualities better adapted to the uses to which it is applied, are very extensively employed. These alloys supply all the varieties of *brass*, a gold-coloured alloy called *Prince Rupert's metal*, *mosaic gold*, *Bath metal*, *the button metal of Birmingham*, *red brass* or *tombac*, *Dutch foil*, *pinchbeck*, *similor* and *Mannheim gold*. Bronze, bell metal, the cymbals, gongs, and *tam-tams* of the Chinese are severally alloys of copper and tin. The specula used in reflecting telescopes consist also principally of copper and tin.

591. METALLURGY OF COPPER. The ores of copper consist of the native metal, its red and black oxides, and its carbonates, but most and chiefly its sulphuret, which is generally combined with that of iron, forming copper pyrites, Cu_2S, Fe_2S_3. Ores called *gray copper*, which are multiple sulphurets of arsenic, antimony, and copper, usually containing more or less iron and zinc, are also worked. These ores contain also silver in sufficient quantity to render its separation profitable.

The ore is disembarrassed of its matrix by mechanical processes. One part of the sulphur is then volatilised by roasting, and another part is either separated as sulphurous acid, or enters into combination with the oxides to form sulphates of iron and copper, which are separated by washing. On leaving the water in which this washing takes place to stand, the copper is precipated, and then submitted to the operations of refining.

In the process of roasting, the arsenic is separated, partly as arsenious acid, and partly as a sulphuret. The remainder forms metallic arseniates. The iron and copper are each partially oxidated, a certain quantity of pyrites escaping the oxidating reaction. The roasted ore is then fused with charcoal and silicious matter. A part of the oxide of copper is reduced, and the metallic copper resulting combines with the undecomposed sulphurets to produce a matter called *matt*. Meanwhile the oxide of iron combines with the silica to form a silicate, which is not reducible by charcoal. These reactions depend on the comparative intensity of the affinities of copper and iron for sulphur and oxygen. The affinity of copper for sulphur is greater than that of iron; while the affinity of iron for oxygen is greater than that of copper, especially in the presence of silicic acid. The silica introduced plays an important part, therefore, in the process of reduction. It enters into combination with the protoxide of iron, which is a very powerful base, producing a silicate not reducible by carbon, and thereby prevents the iron from being mixed with the reduced metal. Meanwhile the oxide of copper is reduced by the charcoal, and surrenders all its metal to the *matt*. Thus by the reaction of the silica and charcoal, the copper remains in the matt, while the iron passes into the scoriæ.

The succession of operations by which these effects are produced are thus enumerated: 1°, the calcination of the ore; 2°, the fusion of the ore thus calcined; 3°, the calcination of the resulting *coarse metal*, or *first matt*; 4°, the fusion of this matt; 5°, the calcination of the *fine metal*, or *second matt*; 6°, the fusion of the matt thus calcined; 7°, roasting of the coarse copper; 8°, refining and toughening the copper.

When the ores are rich, they are sometimes calcined by roasting them several times successively in square stalls, formed by three walls of masonry, *fig.* 141, and completed by a dry stone wall in front. The back wall is pierced with openings under *o*, *o*, to supply the draught. The matt roasted in the first stall is transferred to the next, where it is again roasted, and so on from stall to stall until its calcination is complete.

The poorer and more abundant ores, consisting of copper pyrites mixed with a large proportion of iron pyrites, and but little oxide of copper, are generally

calcined in reverberating furnaces, *figs.* 142, 143, constructed on a scale of great magnitude, the length and breadth of the sole A, being often as great as 24 feet.

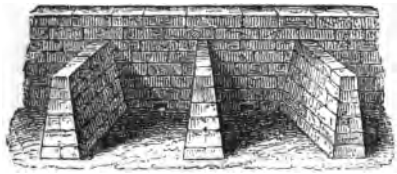
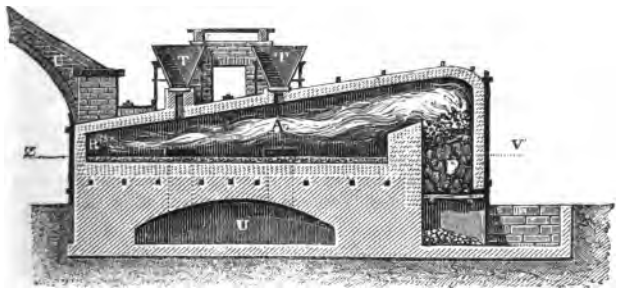


Fig. 141.

Fig. 143 is an horizontal plan at the level of the grate F, and *fig.* 142, a vertical section through the line X, Y. Five doors are provided, one for the fire-place, and

Fig. 142.



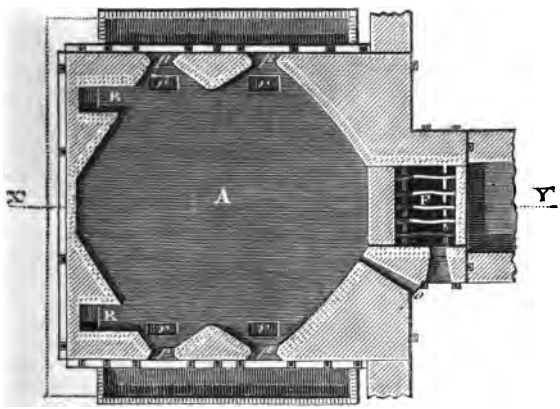


Fig. 143.

the other four, *p*, *p*, *p*, *p*, for working the ore. The furnace is charged with ore by two hoppers T, T, in the upper vault, furnished with valves.

The fusion of the ores is effected also in reverberating furnaces in which a higher temperature is maintained by a more powerful draught. One of these

is shown in plan in *fig.* 144, and in section in *fig.* 145. The roasted ore, mixed with rich scoriæ resulting from preceding operations, and raw ore, rich in

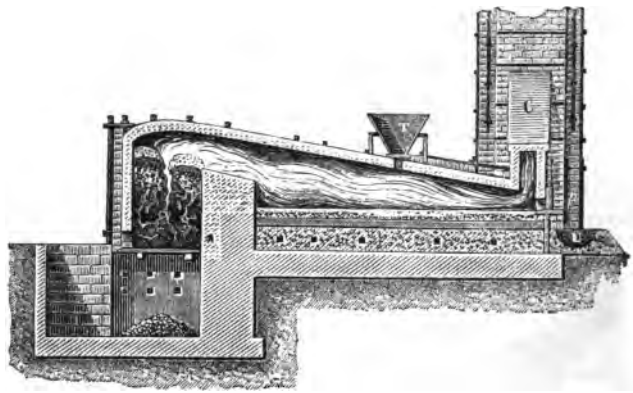


Fig. 145.

oxides of copper, with the addition of a certain quantity of fluor spar to act as a flux, being deposited in the furnace, is submitted to its action for 4 or 5 hours, after which the workman removes the scoriæ floating on the surface

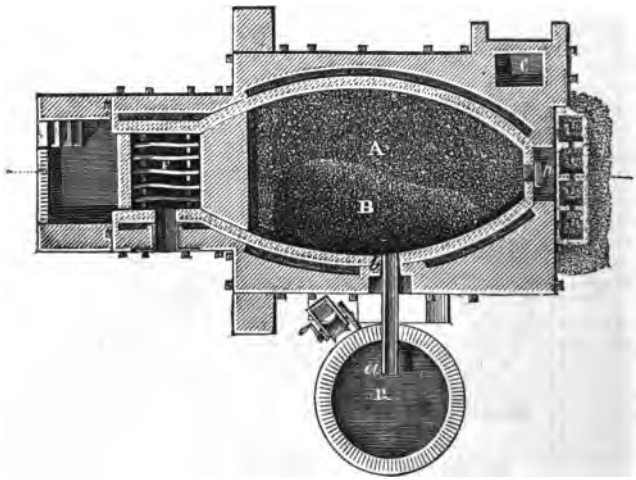


Fig. 144.

with his rake through the door *p*. These scoriæ fall into the cavities U, and the matt in fusion is allowed to flow out through *b*, *a*, into an iron pot R, filled with water, where the metal is granulated. These furnaces, like the former, are fed by hoppers, T, at the top.

The metal which finally results from this process, called *black copper*, is then submitted to the process of refining, by which it is converted into *rosettes*, or fine copper.

CHAPTER XVII.

MERCURY.—SILVER.—PLATINUM.—GOLD.

MERCURY.

592. MERCURY, the only metal liquid at common temperatures, is nearly as white and brilliant as silver, having however a slightly bluish tint. It freezes at —39°, and boils at 620°. There is therefore a large range of the thermal scale between its freezing and boiling points, and it is on this account, as well as others, that it has been selected as the most suitable liquid for thermometers. In freezing it crystallises in octohedrons and suffers a great contraction of volume.

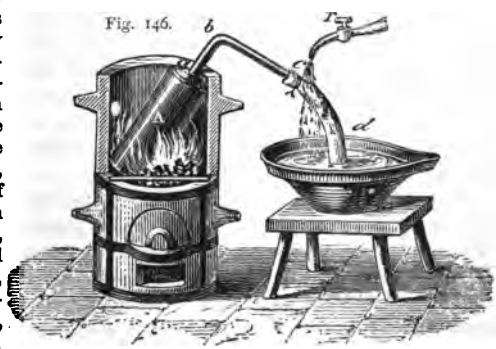
During the voyage of Sir E. Parry in the North Seas its physical properties were submitted to examination in the solid state, and it was found that it holds a place beside lead and tin as to its malleability, ductility, and tenacity. These observations were subsequently confirmed by Thilorier, who, submitting it to the cold produced by a mixture of solid carbonic acid and ether, ascertained that it could be rolled and coined into medals, some of which were actually struck at the French Mint.

Congealed, it produces, when touched, the same sensation and the same effect upon the skin as red-hot metal.

It has neither odour nor taste; is highly dilatable, and uniformily so between the freezing and boiling points of water. At 32° its SG = 13·596, which augments to 14·391 when it is congealed. It absorbs both air and moisture, which, as well as some other impurities, may be expelled from it by heat and distillation.

593. This process of purification may be conveniently performed in the cylindrical wrought-iron bottles, in which the mercury of commerce is sold. One of these, being half full of mercury, is placed in a furnace. A tube, formed of several doubles of linen cloth, is attached to its extremity *c*, *fig.* 146, and received in a dish, *d*, containing cold water. A constant stream of cold water is let fall upon this cloth from *r*. As the distillation of the metal proceeds, its vapour is condensed

Fig. 146.



by the cold cloth, and the liquid metal falls into the dish *d*. In the laboratory, however, this distillation is more commonly made in a glass retort.

The purification effected by distillation is imperfect, since several of the metals usually combined with the mercury pass over with it in the state of vapour, and being condensed, are still mixed with the distilled mercury. When mercury chemically pure is required, a further process is necessary, which consists in pouring into the mercury, at about 140°, common nitric acid, diluted with twice its volume of water. This mixture is allowed to stand at least for 24 hours, being stirred from time to time. The nitrate of mercury is first produced, which is again decomposed by the other metals present. These metals are dissolved, and the pure mercury is precipitated. The purification may be effected by this process alone without distillation.

Mercury gives sensible vapour at 70° to 80°; but not at lower temperatures.

594. When pure it does not wet a body immersed in it. This property may be considered as a practical test of its purity, for when it holds in solution other metals, such as copper, tin, or lead, it then moistens the surface of glass. When globules of impure mercury roll upon glass, they leave behind them a gray pellicle adhering to the surface.

595. Pure mercury, contained in a glass tube, has a convex surface, owing to a repulsion between the glass and the liquid metal; but if it be amalgamated with one part of lead to 4000 of mercury, the surface in the tube will be plane. This expedient is consequently used in graduating glass tubes which hold mercury.

596. When mercury is mixed with fat bodies it assumes a dark gray colour, and appears as a blackish substance, which several chemists regarded as the protoxide; but which, in fact, is nothing more than mercury in a very minute state of subdivision.

Heated in contact with air to the temperature of 660°, mercury is oxidated, the result being the protoxide HgO.

It does not decompose water at any temperature. Nitric acid attacks it cold, producing the nitrate of the protoxide when the mercury is in excess; but when hot, and when the acid is in excess, it produces always the nitrate of the peroxide.

597. Dilute sulphuric acid has no action on it; but when concentrated and warm it dissolves it, disengaging sulphurous acid and forming the sulphate, either of the protoxide or suboxide, according to the proportions of the acid and the metal. It is not sensibly attacked by gaseous hydrochloric acid. If air intervenes, water and the chloride of mercury are formed. It combines with a great number of the other metals, the alloys being called *amalgams*.

598. Chemists differ as to the equivalent of mercury; some taking for it 100 and others 200, which produces a corresponding difference in the formulæ expressing its compounds, some using Hg to express what others indicate by Hg_2. There is a corresponding discrepancy in the nomenclature, what is called the *protoxide* by some being called the *suboxide* by others, and the *peroxide* of some being the protoxide of others. This requires attention in studying different works.

599. THE OXIDES, as we shall denominate them, are the *suboxide* Hg_2O, and the *protoxide* HgO, the equivalent being assumed as Hg = 100.

600. THE SUBOXIDE Hg_2O, called also the gray oxide, may be obtained by precipitating one of its salts, as for example the nitrate Hg_2O,NO_5, by caustic potash. The result is—

$$Hg_2O,NO_5 + KO = KO,NO_5 + Hg_2O.$$

It is a black or dark olive powder, which, being very insoluble, is easily decomposed, giving mercury and the protoxide :—

$$Hg_2O = HgO + Hg.$$

It forms, with acids, well characterised and crystallisable salts.

601. THE PROTOXIDE, HgO, is formed when mercury, raised to a high temperature, is exposed to the air, or oxygen. It is differently coloured, red or yellow, according to the process of preparation. If it be obtained by the calcination of the nitrate of the protoxide it is red, and if by that of the suboxide orange yellow.

The red or protoxide is used in medicine, being a constituent of several ointments, and especially of those prescribed for sore eyes.

602. THE SALTS of mercury are capable of volatilisation or decomposition by moderate heat. The more oxidable metals, such as zinc, iron, copper, tin, and lead, precipitate mercury from its solutions generally in a state of amalgam. The protochloride of tin reduces the salts of mercury with facility.

The presence of organic matter often conceals the reaction of these salts, but copper always precipitates mercury in the metallic state.

Heated with potash, soda, or lime, these salts are decomposed and the fluid mercury is separated so as to be easily distinguished from all the other metals.

Each of the oxides of mercury gives a series of salts.

The neutral salts of the suboxide are colourless, but assume a yellow tint when they become basic.

Some of them are decomposed by water, when an acid salt is produced which remains in solution, and a basic salt, which is precipitated. The reagents commonly used to detect the salts of the suboxide are hydrochloric acid and the alkaline chlorides. These produce a white precipitate of the subchloride of mercury, insoluble in water and the acids, but soluble in chlorine, and blackened by ammonia.

The salts of the protoxide are colourless; the basic salts are yellow.

603. THE SUBCHLORIDE, Hg_2Cl, called in medicine *calomel*, is white, anhydrous, and insipid. It crystallises in four-sided prisms terminated by four-sided pyramids It is volatile, but less so than the protochloride. It is insoluble in cold water and alcohol. One part is soluble in 12000 of boiling water. Its SG = 7·156. The alkalies render it black. The alkaline chlorides and sal-ammoniac, especially in the presence of organic matter, resolve it into mercury and the protochloride. These reactions have great importance in relation to the medical application of calomel.

It is decomposed, producing the protochloride by light, by chlorine, aqua regia, hydrochloric and nitric acids.

Calomel is used in medicine as a vermifuge and a purgative, and also in venereal and scrophulous infections.

604. It may be prepared by heating a mixture of common salt and sulphate of suboxide of mercury :—

$$NaCl + Hg_2O,SO_3 = NaO,SO_3 + Hg_2Cl.$$

605. PROTOCHLORIDE OF MERCURY, HgCl, commonly known as *corrosive sublimate*, is a satiny, white transparent body of a bitter and disagreeable flavour, which reddens litmus, and is a violent poison. It is more volatile than the subchloride, and is soluble to a certain extent in water, but more so in alcohol. Sulphuric acid dissolves it easily. Its crystals, obtained by evaporation in water and alcohol, have right rhomboidal prisms as their primitive forms, while those obtained by sublimation are rectangular octohedrons. In both cases the crystals are anhydrous. Triturated with mercury it is changed into the subchloride. At common temperatures it is decomposed by zinc, iron, and copper. It is not decomposed by sulphuric acid, or, at least, this acid acts upon it with great slowness, even when heated. Nitric and still more hydrochloric acid easily dissolves it without decomposition. The bicarbonates form in a solution of the protochloride a white precipitate of oxychloride of mercury, which soon becomes dark red.

Corrosive sublimate is used in medicine, but it is a dangerous remedy, which requires to be administered with the greatest prudence. It is used also to preserve preparations and to protect wood from insects.

606. THE CYANIDE, HgCy, is a white anhydrous body, which crystallises in anhydrous prisms, having square bases, sometimes opaque and sometimes transparent. It has the taste of the salts of mercury, and is an active poison. Mercury has so strong an affinity for cyanogen that the oxide of mercury decomposes all the cyanides, even that of potassium.

607. To prepare the cyanide of mercury, hydrocyanic acid is put in contact with the oxide of mercury, when the two bodies enter into combination, with disengagement of heat, forming water and the cyanide.

608. THE SULPHURETS of mercury correspond in composition to the oxides, the subsulphuret being Hg_2S, and the protosulphuret HgS.

If a current of sulphuretted hydrogen be transmitted through a solution of the subacetate of mercury, a black precipitate will be obtained, which will be the *subsulphuret* Hg_2S :—

$$HS + Hg_2O = Hg_2S + HO.$$

But if the temperature be raised, this precipitate will be rapidly converted, even in water, into the *protosulphuret*, HgS, and metallic mercury :—

$$HS + Hg_2O = HgS + Hg + HO.$$

If a current of sulphuretted hydrogen be transmitted through a salt of the protoxide or through the protochloride, the first result will be a white precipitate, which will be a compound of the protosulphuret and the salt submitted to the reaction. Thus, the sulphate and nitrate of the protoxide, and the protochloride give severally—

$$2HgO,SO_3 + HS = HgS,HgO,SO_3 + HO,SO_3.$$
$$2HgO,NO_5 + HS = HgS,Hg,NO_5 + HO,NO_5.$$
$$2HgCl + HS = HgS,HgCl + HCl.$$

But if the current of sulphuretted hydrogen be continued until the liquor is saturated, the precipitate previously white will become black, and will then be completely transformed into the protosulphuret HgS.

609. If this *black* sulphuret be heated in a retort it will be sublimed, without any change of composition, but will then become a *red* powder of crystalline fibrous texture. In this state it is the substance well known as *cinnabar*.

610. If mercury be bruised up with sulphur, a substance of like composition but of a *black* colour will be obtained, known in medicine as *mineral ethiops*.

611. The sulphuret, HgS, is found native, usually in compact masses of a dark red colour, and occasionally in transparent bright red rhombohedral crystals. This is the principal ore from which mercury is derived.

Under the common pressure of the atmosphere, cinnabar volatilises without fusion, producing a yellowish-brown vapour, whose SG = 5·4. The solid cinnabar has SG = 8·1 at common temperatures.

612. The sulphuret, HgS, may be obtained with a brilliant red colour, finer than that of cinnabar. In this state it constitutes the pigment known as *vermilion*.

613. Mineral ethiops is converted into cinnabar by sublimation. Being raised to a red heat, it is sublimed and condensed in a cold vessel. Cinnabar bruised up with water and reduced to a very fine powder gives vermilion. The Chinese vermilion, so remarkable for its fine colour, is, however, prepared by the humid way, by the reaction of sulphur on mercury in an alkaline solution.

Vermilion is often adulterated with minium (red lead), colcothar, pulverised brick, or sulphuret of arsenic. The presence of the first three may be detected by raising the mixture to a red heat, when the pure sulphuret of mercury alone will be volatilised. The arsenic may be easily detected by the garlic odour it exhales when heated on charcoal.

614. THE IODIDES, Hg_2I and HgI, correspond in their composition to the oxides and sulphurets.

615. THE SUBIODIDE, Hg_2I, is obtained by triturating iodine and mercury together in the proper proportions with a little alcohol, or by adding iodide of potassium to a solution of the suboxide of mercury :—

$$Hg_2O + KI = KO + Hg_2I.$$

This is a greenish-yellow heavy insoluble powder, which may be sublimed, but is apt to be decomposed by heat, and still more by light, being resolved into mercury and the periodide :—

$$Hg_2I = HgI + Hg.$$

616. THE PROTOIODIDE, HgI, is obtained by treating together iodine and mercury, in the proper proportions, with alcohol, and subliming, or by adding the iodide of potassium to a solution of corrosive sublimate :—

$$HgCl + KI = KCl + HgI.$$

It is an insoluble powder of a brilliant scarlet colour superior to that of vermilion, but loses part of its brilliancy when it is exposed to light under certain conditions. It is insoluble in water, but a hot solution of the nitrate of the protoxide dissolves it, and in cooling deposits fine red crystals.

When heated it undergoes a remarkable change, the red powder, which has an earthy appearance, changing to yellow crystals, and upon a further increase of temperature melting and subliming in yellow rhombic tables. If either of these be agitated or triturated, or even touched with a sharp point, they instantly become red—the red colour beginning at a certain point and spreading gradually through the mass. This phenomenon must be ascribed to a change of molecular arrangement, since the composition of the red and the yellow iodide is precisely the same.

The bromides of mercury are very similar to the chlorides.

617. AMALGAMS is the name given to alloys of mercury with other metals. They are liquid when the mercury predominates, but solid when the metal with which it combines is in a larger proportion. A very small quantity of metal combining with mercury changes altogether its fluidity and other physical properties.

The amalgams of potassium and sodium are produced with disengagement of heat, are pasty, and decompose water. Those of lead and tin have a consistency which varies according to the proportions of the metal. If these amalgams are heated so as to render them perfectly liquid and left to slow cooling, crystals of amalgam are formed, consisting of definite proportions of the metals. The amalgam of silver is found native, crystallised in regular dodecahedrons, its usual composition being Hg_2Ag.

618. THE SILVERING OF MIRRORS consists of an amalgam of tin, and is performed in the following manner: A sheet of leaf tin, equal in dimensions to the glass to be silvered, is provided, and spread upon a marble table framed with wood and surrounded by grooves. This table is mounted, so as to be capable of being inclined more or less in different directions. It is first rendered perfectly horizontal, and a sheet of tin is evenly spread upon it.

Mercury is then carefully poured over it, so as to form a stratum of about the fifth or sixth of an inch in thickness. The edge of the plate to be silvered is next laid upon the edge of the table and lowered gradually, so as to form a continually decreasing angle with the table. By this means it pushes before it the accumulated mercury, which falls into the grooves which surround the table. The glass then being moved parallel to its own frame pushes away a great part of the mercury, leaving no bubbles of air between it and the leaf of tin, so that all the impurities which may be found upon the surface of the mercury are also expelled. The glass is then covered with blocks of plaster of Paris, distributed uniformly over its surface, and the table is inclined to facilitate the escape of the mercury pressed out by the glass. The plate of glass is thus left to itself for two or three weeks, after which it is removed. The tin-foil, now converted into an amalgam consisting of four parts of tin and one of mercury, permanently adheres to it.

619. METALLURGY OF MERCURY. The principal ore of this metal is its sulphuret, called cinnabar, which is found in two different geological formations. It sometimes forms veins in the most ancient transition rocks, and is sometimes disseminated in beds of sandstone, schist, and compact limestone, which appear to belong to the Jurassic period. The celebrated quicksilver mines of Almaden, in the province of La Mancha in Spain, consist of seams of tin so much as fifty feet thick, which traverse the transition rocks of micaceous schist. The quicksilver mines of Idria, in Illyria, present an example of the other class of deposit. Mercury is also sometimes found native in little globules in the bituminous strata. It is always, however, thus found in the neighbourhood of veins or beds of cinnabar, and probably proceeds from some chemical reaction which takes place in that ore.

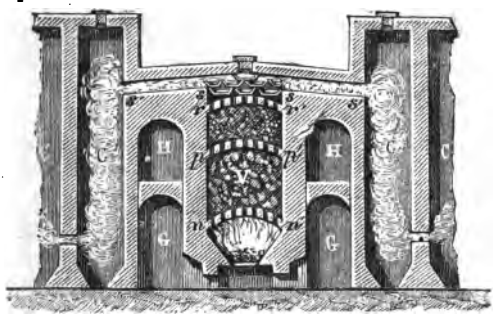


Fig. 148.

The extraction of mercury from cinnabar consists in roasting the mineral in a distilling apparatus. The sulphur burnt is converted into sulphurous gas, and the mercury liberated is distilled and collected in condensers. The apparatus used for this purpose in the Illyrian mines consists of a great roasting furnace, shown by two vertical sections in *figs.* 147 and 148, having on both sides a series of condensing chambers, C C and D D. The ore, in large pieces, is heaped over a vault (n' n'), pierced with a great number of openings, until the chamber V is completely filled. Upon the second vault (p' p') the ore in smaller morsels is placed; and, in fine, upon the third vault (r' r') the ore in dust and the residuum of the preceding processes are deposited. This pulverulent ore is placed in earthen capsules, with which the interior space above r' r' is filled. When the kiln is thus charged, the fire is lighted and the tempe-

rature gradually raised. The mercury is roasted in a current of oxidating air, which enters the ovens through small passages opening into the chambers G H. The vapour of the mercury is drawn into the condensing chamber C C C. The greatest part of the metal is condensed in the first three chambers, from whence it flows in streams (*a b c d*, *a' b' c' d'*, *fig.* 149), which conduct it into a reservoir. In the last chambers much water and but little mercury is condensed: as this is mixed with much dust, it is collected in a separate stream, and then purified by filtration, the residuum being deposited in the upper division *s s'*. To condense the mercurial vapour in the last chambers E D, water is supplied

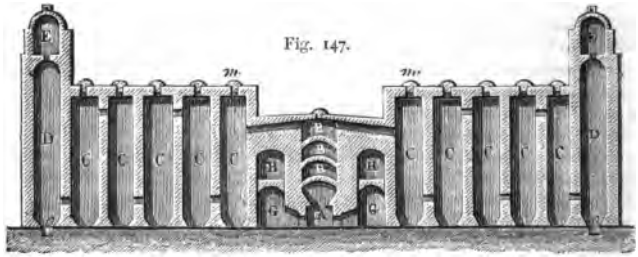


Fig. 147.

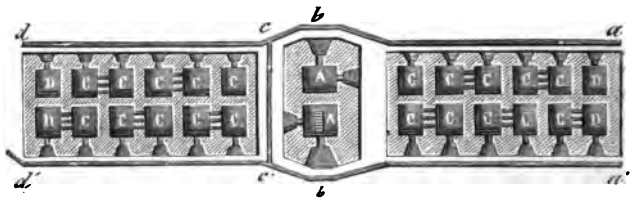


Fig. 149.

upon inclined surfaces, which are extended from one side to the other, between which the gas and vapours circulate before they are allowed to escape into the atmosphere.

The mercury is then filtered through ticken, and deposited in wrought iron bottles for the market. Each of these bottles contains about 60 lb.

SILVER.

620. SILVER is the whitest and most lustrous of the metals. When it has been precipitated from a solution by another metal, it is presented in the form of a white spongy mass, consisting of crystalline grains, which can be consolidated by pressure or hammering. When it is melted and left to cool slowly, it crystallises either in large octohedrons or cubes. It has neither smell nor taste, is a little harder than gold and softer than copper. By an alloy with a small proportion of copper, it acquires increased hardness. Next to gold, it is the most ductile and malleable of all metals. In tenacity it holds the fourth place. A wire, a line in diameter, will support a weight of 180lb. without being broken.

It is a little less heavy than lead, its SG = 10·4743, which is increased by hammering to 10·542. It is fusible at a red heat, and is little volatile, but may be vaporised, either by the oxy-hydrogen blowpipe, or a strong burning lens.

The waste of silver in all works where great quantities of this metal are used, is diminished or avoided by connecting the furnace in which it is fused with flues in masonry from 80 to 100 feet long, which before entering the chimney, communicate with large chambers, where the argentiferous dust is collected, and from which it is from time to time withdrawn.

When silver is fused in an earthen crucible, metallic globules are often seen adhering to the cover, which proceed from the volatilised metal condensed upon it.

Silver is not oxidated in the air, whether dry or humid. It is only tarnished in air under the influence of sulphurous vapours. In a spongy state it is rendered incandescent by a current of hydrogen, when raised to a temperature somewhat above that of boiling water; a phenomenon which belongs to the same class as the well known one presented by spongy platinum. Lucas has shown, that pure silver kept for some time in a state of fusion, has the property of dissolving a certain quantity of oxygen, which it evolves when solidifying. Gay Lussac has shown that the volume of oxygen thus absorbed, may amount to 22 times that of the silver. The presence of a small proportion of copper deprives silver of this singular property. Silver does not dissolve nitrogen.

621. Silver is attacked by but few of the acids. Its best solvent is nitric acid, which produces nitrate of silver and nitric oxide :—

$$3Ag + 4(NO_5,HO) = 3(AgO,NO_5) + 4HO + NO_2.$$

622. Sulphuric acid, when dilute, has no action on silver; but when concentrated, dissolves it. Phosphoric acid attacks it only in the dry way. Hydrochloric acid, when concentrated and hot, has a sensible action upon it, especially if it be in contact with platinum, producing the subchloride of the metal and disengaging hydrogen. Aqua regia converts metallic silver into the chloride.

623. Hydrosulphuric acid attacks silver at common temperatures, transforming it into a sulphuret. A plate of silver plunged in a solution of this acid is immediately blackened.

The vegetable acids have no effect upon silver. It is not altered by the caustic alkalies, carbonates, nitrates, or alkaline chlorates. Silver crucibles are, therefore, used in acting on the silicates by these different substances. When an alkaline silicate is kept in fusion in a silver crucible, a small quantity of oxide of silver is formed, which colours the silicate yellow.

The continued contact of silver with common salt in a state of fusion, produces a sensible quantity of chloride of silver.

Silver in subdivision heated with oxide of copper, CuO, plumbic acid, minium, the peroxide of manganese, and other oxides, reduces these to a lower state of oxidation.

624. Silver enters directly into combination with sulphur, selenium, phosphorus, and arsenic. It absorbs chlorine but slowly. A solution of sea salt in contact with air, will dissolve a certain quantity of silver, producing a double chloride of sodium and silver, the liquor being rendered alkaline; a fact which explains the action manifested on silver vessels in which solutions of the alkaline chlorides are boiled.

It combines directly at common temperatures, with bromine and iodine, and forms alloys with most of the metals.

625. THE OXIDES are: 1°. the suboxide, Ag_2O; 2°. the protoxide, AgO; and, 3°. the peroxide, AgO_2. If certain salts formed by the combination of organic acids with the protoxide, be raised to 212°, the protoxide will dismiss half its oxygen, and a subsalt of silver, Ag_2O,A' will remain. This salt produces in water a brown solution, from which the suboxide, Ag_2O is precipitated in the form of a black powder.

The protoxide, the only oxide which has much interest, is obtained by pouring an excess of potash into a solution of the nitrate of silver, when the hydrate of the protoxide is produced as a light brown precipitate, which loses its water, either in a dry vacuum, or by a moderate heat, and is changed into an olive-coloured powder which is the anhydrous protoxide.

The protoxide is a powerful base, which completely saturates the strongest acids. It is slightly soluble in pure water. The solution having an alkaline reaction, renders green the tincture of violets and restores the colour of litmus reddened by an acid. It is completely insoluble in potash and soda, is dissolved by the vitreous fluxes and colours them yellow. All its oxygen is set free on a slight elevation of temperature, the metal remaining. It is decomposed under the influence of light, and changed into a black substance, which may be either silver in a state of minute subdivision, or the suboxide.

626. FULMINATING SILVER is a compound of ammonia with the oxide of silver. It is prepared by putting in contact for some hours a concentrated solution of ammonia with oxide of silver, recently precipitated and still moist. The oxide becomes black and the liquid is then decanted. Small quantities of the black powder thus formed, are then placed on pieces of unsized paper and left to dry. Fulminating silver may also be obtained by dissolving the nitrate of silver in ammonia and precipitating the liquor by potash.

Fulminating silver compressed by a hard body, even when still humid detonates with violence. It fulminates even under water when submitted to friction,

and may produce the fracture of the vessels which contain it. When dry, it detonates by the mere contact of a feather. It is very soluble in ammonia. This solution is spontaneously decomposed, depositing metallic silver and disengaging nitrogen. The composition of fulminating silver has not yet been certainly determined.

627. THE PEROXIDE, AgO_2, is obtained by decomposing a very dilute solution of the nitrate of silver by the voltaic pile. It is deposited upon the positive pole in prismatic crystals of a blackish gray colour and a metallic appearance. It is insoluble in water, and resists the temperature of boiling water, but is decomposed at 300°, being resolved into metallic silver and oxygen. It forms with sulphur and phosphorus, detonating mixtures.

628. The acids saturated with oxygen, such as sulphuric, nitric, and phosphoric, dissolve it, disengaging oxygen and producing salts of the protoxide of silver. Sulphurous and nitrous acids, and others, are changed into sulphuric and nitric acids which then combine with the protoxide :—

$$AgO_2 + SO_2 = AgO, SO_3.$$

Hydrochloric acid by contact with the peroxide produces water, chlorine, and chloride of silver :—

$$AgO_2 + 2HCl = 2HO + Cl + AgCl.$$

629. THE SALTS of silver are formed almost exclusively from the protoxide, the peroxide not combining with the acids, and the suboxide only in exceptional cases with certain organic acids, forming salts of no importance and but little known.

The salts of the protoxide, AgO, are colourless when formed by an acid which is itself colourless. They have an acid, astringent, and metallic taste, and are poisonous. Light blackens them, partly reducing them, and they are generally decomposed under the influence of heat. Several are neutral to the colour test. They are precipitated by hydrochloric acid and the chlorides, even in the presence of organic matter. This is their most sensitive test. The hyposulphite is, however, an exception.

Phosphorous and hypophosphorous acids reduce them, especially when hot. They are reduced very promptly before the blowpipe when mixed with soda.

In their solutions, potash, the ferridcyanide of potassium, and the chromate of potash, give brown or red precipitates; ammonia precipitates the oxide; the carbonates of potash and ammonia, pyrophosphate of soda, oxalic acid, ferrocyanide of potassium, hydrochloric acid and the chlorides, iodide of potassium and sulphate of the protoxide of iron, give white precipitates; phosphate of soda, a yellow precipitate; zinc precipitates metallic silver; and tannin and the chlorate of potash give no precipitate.

630. THE CHLORIDE, AgCl, as obtained in the humid way, is curdy and dense. When suspended in water, it is collected by agitation or the action of heat into a curdy mass of the greatest whiteness. It is rapidly changed when exposed to direct solar light, being rendered brown and disengaging chlorine. It is then transformed into the sub-chloride, Ag_2Cl. When kept in a flask

with moist chlorine and exposed to the light it remains white. It is fusible at 500°, being converted into a yellow liquid which in cooling becomes translucent, presents the appearance and consistency of horn, and can be cut by a knife. When fused it passes through the crucible like litharge. Though difficult to be distilled, it is volatilised when fused. It is not decomposable by heat. Pure carbon does not decompose it ; but hydrogenised carbon reduces it, producing hydrochloric acid. It is also reduced by carbon in the presence of aqueous vapour, hydrochloric acid, oxygen, and metallic silver being formed :—

$$AgCl + HO = HCl + Ag + O.$$

Most of the metals reduce the chloride by the dry way, such as iron, zinc, tin, antimony, bismuth, lead, copper, &c. Mercury, however, decomposes it only imperfectly.

Iron and zinc reduce it when dry and at common temperatures. The other metals separate the silver only in the presence of dilute hydrochloric acid.

Nitric acid does not sensibly dissolve it. Hydrochloric acid concentrated and boiling, dissolves it in a small quantity. It is deposited in octohedral crystals by evaporation in the liquor. Concentrated sulphuric acid decomposes it slowly. Caustic potash and soda are without action upon it when cold ; but at the temperature of boiling water, they decompose it promptly.

631. The chloride of silver exists native. It is of a pearly gray colour, which often passes to lavender blue or violet. It becomes brown in the air. Its lustre is that of the diamond and it is generally translucent. It is flexible, malleable, and soft, and is found crystallised in cubes, and its SG = 5·55. Its composition is identical with that of the artificial chloride.

632. The Sulphuret, AgS, is found sometimes in powder, sometimes in amorphous tarnished masses of leaden gray colour, and sometimes in cubes, or octohedrons of metallic lustre and SG = 7·2. It is more fusible than silver, soft enough to be scratched with the nail, and so malleable as to receive an impression like a medal. Medals, indeed, have been struck with this sulphuret. When roasted it gives sulphurous acid and metallic silver :—

$$AgS + 2O = Ag + SO_2.$$

Hydrogen and most of the metals reduce it at a moderate temperature. The reduction is especially easy with zinc, lead, and copper.

Concentrated and boiling hydrochloric acid transforms the sulphuret into the chloride and hydrosulphuric acid :—

$$AgS + HCl = AgCl + HS.$$

Nitric acid attracts it very slowly. Concentrated sulphuric acid, on the contrary, decomposes it rapidly when warm, producing hydrosulphuric acid and sulphate of silver :—

$$HO,SO_3 + AgS = AgO,SO_3 + HS.$$

It combines with a great number of metallic sulphates.

633. The sulphuret is obtained artificially, by precipitating a salt of silver, by hydrosulphuric acid, or a soluble sulphuret. It may also be obtained by heating silver with sulphur.

634. It is found native in abundance, and constitutes the principal ore of silver. It sometimes forms thick veins, in the primitive rocks and in the lower secondary strata. The principal silver mines of Europe are those of Friburg in Saxony, of Hungary, and Transylvania. The chief silver mines in South America are in Guanaxuato, Catorre, and the Serra del Potosi.

635. THE NITRATE, AgO,NO_5, the most important and best known of the salts of silver, crystallises in square, colourless, and transparent plates, which are unalterable in the air. It is dissolved by its own weight of cold, and by half its weight of boiling water. Alcohol dissolves a fourth of its weight of this salt when warm, and a tenth when cold. Light decomposes it, but only in the presence of organic matters. It corrodes the skin, producing spots of a dark violet colour, which are removed by cyanide of potassium. When pure it has no action on litmus paper, reddening it only when it contains free nitric acid.

It is fusible below a red heat without decomposition, and forms in cooling, the crystallised substance called *lunar caustic* used in surgery.

At a red heat it is decomposed, being reduced first to the nitrite, and then to metallic silver. Thrown upon burning charcoal it burns briskly, leaving a metallic coating. A mixture of this salt with sulphur or phosphorus detonates. Phosphorus reduces its solution in the cold. Carbon also reduces it, but only when warmed and under the continued influence of light.

If a linen cloth soaked in a solution of the nitrate be presented to a current of hydrogen a black deposit will be produced upon it, consisting of silver in minute subdivision, which sometimes gives a metallic reflection.

636. A weak solution serves as a marking ink for linen. The linen is previously soaked in starch-paste, rendered alkaline by a small proportion of the carbonate of soda. If the linen be then marked with the nitrate of silver, black indelible characters will be formed on it. It combines with liquid ammonia, producing colourless crystals, whose composition is $AgO, NO_5, 2(NH_3)$.

It combines also with the cyanides of mercury, copper, and silver, the last compound fulminating.

637. This salt may be obtained directly by the action of nitric acid on pure silver.

638. FULMINATE OF SILVER $(AgO)_2(CyO)_2$, is a crystalline powder, imperfectly soluble in cold, but dissolved by 36 times its

weight of boiling water. It has a metallic taste, and is neutral to the litmus test. It is highly detonating.

This salt is prepared by dissolving 2·25 parts of pure silver in 45 of nitric acid at 104°, into which 60 parts by weight of alcohol at 185° is poured, and the mixture boiled. It soon becomes turbid. The liquor being removed from the fire, as much more alcohol is added, little by little. The fulminate being then gradually deposited, is washed upon a filter with distilled water, and dried on a water-bath. The weight of the fulminate thus obtained, is nearly equal to that of the silver employed.

Great care should be taken in the preparation of this salt. The use of rods of glass or other hard bodies should be avoided, since they would produce detonation. While still humid the fulminate is to be divided into several parts to avoid accidents.

639. THE SULPHATE, AgO, SO_3, crystallises in brilliant colourless crystals, the primitive form of which is the rhomboidal prism. Boiling water dissolves about 1 per cent. of its own weight, depositing a part on cooling. This salt is more soluble in concentrated sulphuric acid. Water precipitates it from this solution.

It is decomposed at a red heat. Calcined with carbon it leaves a mixture of silver and the sulphuret of silver.

It is usually prepared by dissolving silver in concentrated and boiling sulphuric acid. This solution in cooling deposits little needles of the sulphate. The mother-waters left to themselves for certain inoxidable metals, such as gold and platinum. Copper may a long time, give octohedral crystals.

640. ALLOYS with a great number of metals are formed by silver; but the only important ones are those of copper and be alloyed with silver by means of fusion in all proportions. These alloys are less ductile but harder and more elastic than silver. They are generally white, and only assume a red tint when the proportion of copper is very considerable.

641. Sulphur heated with an alloy of copper and silver in insufficient quantity to produce the sulphurets of the two metals, attacks especially the copper, the greatest part of which is separated in the state of a sulphuret, taking with it, however, a certain quantity of the sulphuret of silver.

642. PHOTOGRAPHY depends on the property which the salts of silver have of being blackened under the influence of light. A plate of silver or silvered copper is covered with a coat of iodide of silver, AgI, by exposing it to the vapour of iodine. The plate thus prepared is placed in the focus of a lens in a camera obscura, so as to receive upon it the optical picture of objects placed at a distance in front of the lens. The iodide of silver is decomposed more or less completely by the lights and shades of the picture. Its alteration is incomplete in the darker parts, and does not take place at all in the parts absolutely black.

To render the image thus produced on the plate visible, it is afterwards exposed to the vapour of mercury, when an amalgam of silver is formed upon

those parts corresponding to the brighter parts of the image. The plate is then washed in a weak solution of hyposulphite of soda, to remove such parts of the iodide of silver as have not been decomposed, which otherwise would be blackened by exposure to the light.

This process, originally invented by Daguerre, has been improved on by the use of certain substances which accelerate the effect of the light; the vapour of bromine, for example, which renders the coat of iodide of silver more sensitive to the action of light, and causes it to take the image more rapidly. Different processes have also been discovered, by which the impressions produced are rendered more distinct and permanent.

More recently, photographic images in great perfection have been obtained by substituting for metallic plates paper, called *photogenic paper*, prepared with different compounds of silver. The paper is blackened in the luminous parts of the image, and remains white or light-coloured in the more obscure parts. In this state the proof or impression is said to be *negative*, the natural lights and shades being reversed. Such a negative proof is exposed to light by placing it before another sensitive paper, which becomes blackened in the parts which correspond to the white parts of the first, and thus forms a *positive* impression. This latter proof is then washed with a solution of hyposulphite of soda.

643. METALLURGY OF SILVER. As already stated, silver is obtained in considerable quantities in the metallurgic processes applied to certain ores of lead and copper, which however contain so small a proportion of silver that they are not worked expressly for that metal, the extraction of which is merely incidental to the operations by which their principal metallic constituents are obtained.

The ores to which silver is thus merely incidental, are the argentiferous sulphurets of lead and the argentiferous copper pyrites. The silver is separated from these by two processes—*amalgamation* and *cupellation*. In the former process the mercury is so applied as to form an amalgam with the silver, which, being liquid while the copper remains solid, can be easily separated by mechanical means, without the application of heat or chemical agency. The silver is then obtained from the amalgam by distillation. In the process of cupellation, an alloy of silver and lead is obtained, which being submitted to an oxidating agency, which acts on the lead alone, converts it into litharge, which being fused flows off, leaving the silver.

The ores which are too poor in lead and copper to be treated expressly for these metals, and sufficiently rich in silver, are submitted, after some preparatory processes, directly to amalgamation, which is conducted by two methods, the European, in which fuel is used, and the American, which is performed without the application of heat.

GOLD.

644. Gold is a brilliant metal of a reddish-yellow colour, familiar to every eye, and is susceptible of a fine polish. It is capable of being reduced by the goldbeaters' process into thin leaves, through which light transmitted appears green, but when seen by reflection, red. If it be reduced to a very fine powder it has a yellow colour tinged with violet. It crystallises in quadrangular pyramids and octohedrons, and is found native in different

crystallised forms, all of which are derived from the cube. In hardness it is inferior to silver, and almost as soft as lead. The hardness necessary for its use in the arts is obtained by alloying it with a small proportion of copper. It is the most malleable and the most ductile of the metals, and may be reduced to leaves so thin that 250,000 laid one upon the other would not exceed an inch in thickness. It is so ductile that a single grain may be drawn into 700 feet of wire. Its tenacity is inferior to that of iron, copper, platinum, or silver. In passing from the liquid to the solid state it undergoes a much greater contraction than the other metals. Its SG = 19·258 : this, however, is increased by hammering to 19·367. Its point of fusion is about 2000° of the air thermometer. In the liquid state it appears green.

It is almost fixed at the highest temperature which can be obtained in the furnace, but it is sensibly volatilised by a powerful burning lens or the oxyhydrogen blowpipe. When exposed in thin leaves to the action of a powerful voltaic pile it is vaporised. In a state of minute subdivision it becomes incandescent when heated to 120° in a current of hydrogen. It shares with platinum, iron, silver, and some other metals, the property of being weldable. If, after having been precipitated from its solutions by iron, it is washed and strongly compressed by a hydrostatic press, it is changed into a coherent, malleable and ductile mass, which can be forged, rolled, and wire-drawn.

By compressing and hammering a mixture of gold and silver in powder a damasked compound is obtained, which could not be produced by fusing the metals together.

645. Gold is, of all known metals, one of those least affected by chemical agencies. It resists the continued action of air, oxygen, water, and sulphuric, nitric and hydrochloric acids. Selenic acid attacks it, giving up an equivalent of its oxygen, and being converted into selenious acid.

Nitric acid, mixed with hydrochloric, hydriodic, hydrobromic, and other similar acids, forms varieties of aqua regia, which dissolve gold, transforming it into a chloride, iodide, bromide, &c. Gold is also soluble in mixtures of hydrochloric with other acids, such as chromic, sulphuric, &c., which are capable of disengaging chlorine with hydrochloric acid. In general, every mixture which is capable of disengaging chlorine can attack it.

In the arts, aqua regia, consisting of one part of nitric acid and four of hydrochloric acid, is used to dissolve it.

The alkalies do not attack it either by the dry or humid way; but when they are heated with it in contact with air, an absorption of oxygen takes place, and an alkaline aurate is formed.

It is not attacked by the chlorate of potash, but according to

Tennant, nitre in fusion acts upon it. Neither carbon, sulphur nor selenium have any effect on it, even at the highest temperatures. It is not tarnished by hydrosulphuric acid. The alkaline persulphurets attack it by either the dry or humid way, and transform it into a sulphuret.

The alkaline monosulphurets act upon it only in contact with air, and after they have been changed into persulphurets.

Phosphorus and arsenic will combine with it under the influence of heat. Chlorine attacks it even when cold, producing the chloride of gold. Hammered gold is rapidly disolved in an aqueous solution of chlorine. Bromine dissolves it, but iodine has no action upon it.

It imparts to glass a red colour. In a state of minute subdivision it is used for the ornamentation of glass and porcelain. The metal pulverised for this purpose is obtained by precipitating it from its solution by sulphate of protoxide of iron. For certain ornamental purposes it is obtained in subdivision, by bruising gold leaf with honey.

646. To obtain gold chemically pure, the following method has been indicated by M. Levol: A piece of gold is dissolved in aqua regia, composed of 1 part of nitric acid at 20° of the hydrometer, and 4 of the hydrochloric acid of commerce. The liquor is filtered to separate it from the chloride of silver, and an excess of protochloride of antimony is added, dissolved in a mixture of water and hydrochloric acid. The gold is precipitated after the lapse of some hours, especially if the liquor be slightly warmed. The metal appears in the form of small coherent laminæ, which rapidly collect together. It is washed at first with hydrochloric acid, and then with distilled water, after which, it is fused in an earthen crucible with a small quantity of nitre and borax.

647. Oxides. The equivalent assigned to gold by most of the English chemists is 197, while the French chemists, with some few English, take it at half that number. The consequence of this is, that according to the majority of English chemists the two oxides of gold are, AuO, and AuO_3, while according to the French chemists and those who follow them, they are Au_2O and Au_2O_3. We shall here follow the former convention.

648. The protoxide of gold, discovered by Berzelius, has recently been submitted to examination by Figuier. It is presented in the form of a brown or dark violet powder, insoluble, unalterable by light, and not attacked by the most powerful of the oxacids. Dried at 212°, it has a bluish violet colour. At 482°, it is decomposed, being resolved into oxygen and the metal. With hydrochloric acid it forms the perchloride, and deposits metallic gold. With hydrobromic, and hydriodic acids, it forms a protobromide and protoiodide of a dark brown colour. The caustic alkalies dissolve it, but only at the moment of its precipitation. It forms, with ammonia, a fulminating compound.

649. This protoxide may be obtained by decomposing the protochloride by a dilute solution of potash. A part of the protoxide forms a dark violet precipitate, the remainder being dissolved in the alkali, to which it imparts a yellow

colour. It may be precipitated from this alkaline solution in the form of a dark violet jelly, by saturating the liquor incompletely with nitric acid.

650. AURIC ACID when hydrated is sometimes brown and sometimes a pale yellow. It is insoluble in water. Light reduces it rapidly. It is resolved into gold and oxygen at the temperature of 473°. Hydrogen reduces it only by the influence of heat. Carbon and carbonic oxide rapidly reduce it to the metallic state. Boiling alcohol decomposes it, and separates the gold.

Nitric, sulphuric, and acetic acids dissolve it only in small quantities. Water precipitates it from its solutions. Almost all the organic acids reduce it to the metallic state. Oxalic acid produces this reduction very easily, being changed into carbonic acid. Hydrochloric and hydriodic acids dissolve it, producing the chloride or iodide of gold. It is easily dissolved, even in the cold, in potash and soda, producing aurates, which can be crystallised. Ammonia forms with auric acid a fulminating compound.

651. PREPARATION. According to Pelletier, auric acid may be prepared by precipitating the chloride of gold by magnesia or the oxide of zinc. The aurates of magnesia or zinc are thus formed, which are insoluble, and these salts treated cold by dilute nitric acid, are decomposed, giving auric acid.

This acid may also be prepared by boiling for some minutes the chloride of gold with an excess of potash, and then precipitating the aurate of potash by an excess of acetic acid. The hydrated auric acid will thus be obtained perfectly pure, which is soluble in the cold in potash. This solution gives by evaporation *in vacuo*, a crystallised aurate of potash.

The aurate of potash thus prepared is presented in yellow crystals, containing water of crystallisation. When slightly heated it is decomposed, disengaging oxygen, and leaving a mixture of potash and metallic gold.

652. The aurates of potash and soda are soluble in water. Their solution has a brownish yellow colour. These salts are decomposed by the acids and give a yellow precipitate of hydrated auric acid.

653. The aurates of magnesia, zinc, &c., are insoluble in water and may be prepared by double decomposition.

654. FULMINATING GOLD. Two sorts of this compound are known, one of which contains chlorine and the other not.

If auric acid be digested with ammonia a gray compound is obtained which detonates under the hammer, by friction, or by a slight increase of temperature, and even spontaneously. This body, however, can be decomposed without detonation when heated with from 20 to 30 times its own weight of the sulphate of potash, the oxide of copper, or massicot. If the chloride of gold be digested with an excess of ammonia a yellow compound will result which will fulminate like the former. This treated by a mixture of ammonia and caustic potash leaves a mixture, identical with the fulminating precipitate prepared with auric acid and ammonia.

655. PURPLE OF CASSIUS is the name given to the precipitate of a purple red colour, obtained by treating the chloride of gold with a mixture of protochloride and bichloride of tin. This compound has been submitted to extensive researches by chemists, but its

true character has not yet been satisfactorily ascertained. The most probable formula for this body is $AuO,SnO_2,SnO,SnO_2 + 4HO$.

656. THE PROTOCHLORIDE, AuCl, has a pale yellow colour, is insoluble in water, unstable, and is resolved by light, or a low heat, into metallic gold and the perchloride. The alkalies transform it into the protoxide of gold. It is prepared by submitting the perchloride to a temperature of about 300°, chlorine being disengaged, and the protochloride formed.

657. THE PERCHLORIDE, $AuCl_3$, has a reddish brown colour, is deliquescent, crystallising with difficulty. It is very soluble in water and alcohol, its solution having a very dark yellow colour. Under the influence of light it is resolved into chlorine and the protochloride, or into chlorine and metallic gold, according as the temperature is higher or lower. When its solution is agitated with ether two distinct strata are formed; the superior, having a strong yellow colour, consisting of ether holding the salt of gold in solution; the inferior being colourless, and containing only water charged with hydrochloric acid.

658. The solution of chloride of gold in ether was formerly employed in medicine under the name of *potable gold*. It was sometimes used to gild steel. This liquor is spontaneously decomposed, depositing, after a time, metallic gold.

659. Gold is precipitated from its solution in aqua regia with variable colours by a great number of bodies, such as hydrogen, carbonic oxide, carbon, phosphorus, nitric oxide, and almost all the vegetable and animal substances, most of the metals, sulphurous and phosphorous acids, the sulphites, the phosphites, the salts of the protoxide of mercury and of the protoxide of iron.

660. ALLOYS OF GOLD are formed with almost all the metals. It unites directly with manganese, iron, zinc, cobalt, nickel, copper, tin, antimony, bismuth, silver, &c. It alloys in all proportions with copper, which enriches its colour, increases its hardness and fusibility, but diminishes its malleability. The density of the alloy with copper is less than the mean density of the components.

The presence of minute proportions of lead in these alloys renders the compound brittle. The fusibility of the alloy is greater than that of gold, and increases with the proportion of copper. These alloys are, therefore, used for gold solder. The solder known as *red gold solder* consists of 5 parts of gold and 1 of copper.

661. Owing to its softness gold cannot be employed in a state of purity for coinage, medals, or jewellery. Gold for coin is therefore always alloyed, either with silver or copper, generally the latter. The English gold coin contains 917 parts in 1000 of pure gold. The coin of France contains 900 parts in 1000. In France the alloys employed in jewellery and goldsmiths' work are regulated by law. The proportion most commonly used is 750 parts of pure gold in 1000, with a tolerance of a 3000th above or

below this limit. There are two other standards admitted, one of 840, and the other 920 parts in 1000, but these are rarely used.

662. JEWELLERS' GOLD, which contains an undue proportion of copper, is liable to tarnish. Its brilliancy may be restored by passing it through caustic ammonia and washing it with water.

663. AMALGAM. Gold combines readily with mercury, even at common temperatures. A plate of gold exposed to the feeblest mercurial emanation is whitened. This property serves sometimes as a test for the presence of mercury. A piece of gold rubbed with mercury becomes brittle and is easily broken between the fingers. Mercury dissolves a great quantity of gold without ceasing to be liquid, the amalgam having the whiteness of silver. When mercury is saturated with gold, it becomes slightly yellow and acquires the consistency of wax.

664. Gold combines with silver in all proportions. The density of these alloys is nearly the same as the mean density of their constituents. They are more fusible than gold, and harder and more elastic than either gold or silver. They are much employed in jewellery, and bear the names of *yellow gold*, *pale gold*, *green gold*, &c. Green gold, which is the alloy most used, consists of about 7 parts of gold and three of silver. *Electrum* consists of 4 parts of gold and 1 of silver.

665. METALLURGY OF GOLD. Gold is found native, sometimes pure, but most frequently combined with variable quantities of silver. It is usually crystallised in cubes or octohedrons, or some derivative of these forms. It is also found in small grains or spangles, and sometimes, though more rarely, in lumps called *pepitas* or *nuggets*. These are occasionally very large and weighty. Humboldt mentions one found in Peru, weighing 26lb. Another is mentioned as being found in the Oural mountains, weighing nearly 80lb. Nuggets of even greater weight have been found more recently in Australia and California.

The rich mines of Mexico, Peru, Hungary, Transylvania, and the Oural mountains consist of veins of auriferous sulphuret of silver, which traverse the transition rocks.

Native gold, scattered in minute grains and spangles through argillaceous and ferruginous sands, constitute the gold sands, deposited in the beds of rivers, which are frequently worked with profit. The richest deposits of this kind hitherto discovered are those of California. The sands of the Brazilian rivers are less rich in gold, but contain also diamonds, platinum, and other precious deposits.

The metal is extracted either from alluvial deposits or from ores found in mineral veins.

666. WASHING. When contained in alluvial deposits it is separated by the process of *washing*. This is performed by various expedients in different localities, all, however, being effected by transmitting a constant current of water through the pulverised matter in which the precious metal is disseminated. The earthy matter is thus washed away and the metal remains. This is done in many places by spreading the auriferous sand upon an inclined table, cut into transverse parallel grooves down which a stream of water is conducted. The gold grains and spangles, with any other metallic constituent, which may

exist in the sand, fall into the grooves by reason of their great specific weight, while the earthy matter, which contains no metal, is carried off by the stream. The rich matter thus deposited in the grooves, is from time to time removed to be treated by a subsequent process of amalgamation.

667. In the Oural gold-works the auriferous sand is collected in cases having a bottom of sheet iron pierced with holes, about an inch in diameter. A current of water being let flow through these, the workman stirs up continually the sand with a sort of shovel. The finest parts descending through the holes are received upon large inclined tables placed under the cases, which are covered with linen cloth. The sand which descends along the table is swept back continually to the upper part until at length the gold grains mixed with other heavy metallic matters remain. The rich sand thus obtained is again similarly washed, but with still greater care, on smaller tables. The ferruginous impurities are next separated from it by passing magnetised bars through it, to which these adhere, and the remainder is fused in large crucibles of graphite. The gold settles in the bottom of the crucible, covered with a layer of scoriæ, which still contains much gold in a granular state not yet fused. This scoriæ is skimmed off, pounded, well washed, and the residuum fused in small furnaces. The result is an auriferous lead from which the gold is separated by cupellation.

668. In the gold-works of the Tyrol, a certain quantity of the precious metal is obtained from pyrites by amalgamation in mills of the form shown in *fig.* 150.

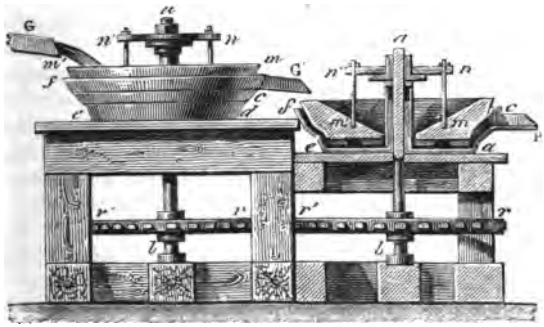


Fig. 150.

Several of these mills are usually placed in a series one below the other, forming thus a sort of cascade. In the figure the superior mill is shown by an external view, the inferior by a vertical section. The pyrites having been pulverised, are mixed with water so as to have the consistency of a turbid liquid; this liquid is allowed to flow by a spout G into the first or uppermost mill *c d e f* from which it passes by the spout G′ into the second, and so on through the series. Each mill consists of a hollow basin, *c d e f*, of cast-iron, fixed upon a wooden table. A shaft, *a b*, passing through a tube, in the centre of this basin is kept in revolution by a toothed wheel *r r′* fixed upon it. This shaft gives motion to a wooden grinder, *m m′*, by the framing *m n*, *m′ n′*. The form of this grinder corresponds to that of the cast-iron basin, from which it is kept at the distance of about an inch by several small feet beneath it. The upper part of this wooden grinder has the form of a conical funnel, into which the turbid auriferous liquid flows, and passes between the grinder and the basin through an opening left round the shaft, for that purpose.

These mills make from 15 to 20 turns per minute. At the bottom of each

about 5olb of mercury is placed so as to form a stratum about half an inch deep, which is constantly agitated by the motion of the feet of the wooden grinder, thus continually stirring up the ore. The gold grains and spangles, as fast as they arrive, are thus dissolved by the mercury, those which escape dissolution in the first mill being dissolved in the succeeding ones. After several weeks' work the mercury is withdrawn, and being filtered through chamois leather, a solid amalgam is obtained, containing about 33 per cent. of gold, which is separated by distillation.

PLATINUM.

669. PLATINUM when forged is nearly as white as silver, and is susceptible of a high polish. It has neither taste nor smell, and is very ductile and malleable. A wire, of a line in diameter, will support the weight of 250lb. It is softer than silver, but rendered hard by a slight alloy of iridium. In hardness it holds a place between copper and iron. It is the least dilatable of all the metals. Its SG = 23·47 to 21·53, according as it has been more or less hammered. Its SG = 21 when cast. It is infusible in a forge fire, but may be fused by the oxyhydrogen blowpipe, and the voltaic current. At a white heat it is softened, and may be forged and welded like iron; a property which renders it highly valuable, inasmuch as various utensils can be made of it. At a high temperature it can be volatilised, and produces brilliant sparks under the blowpipe. It is not oxidised by the air at any temperature, nor does it decompose water under any conditions, and is attacked by few of the acids. Its solvent is aqua regia, consisting of 75 per cent. of hydrochloric acid at 15° of the hydrometer, and 25 of nitric acid at 35°. A hundred parts of this liquid is capable of dissolving two of platinum. It is strongly attacked by potash and lithia, but with more difficulty by soda. A mixture of nitre and potash attacks it briskly, as does also the bisulphate of potash.

670. Several oxides, including even those which are irreducible by heat, attack platinum at a high temperature. Spongy platinum combines with sulphur when sufficiently heated, but forged platinum does so with difficulty. Phosphorus and arsenic also combine with spongy platinum, forming a very fusible phosphuret and arseniuret. When organic matter containing phosphorus, such for example as the brain of an animal, is burnt in a platinum crucible, the phosphuret of platinum is produced by the reduction of phosphoric acid. The crucible is in this manner pierced in a few seconds.

671. Chlorine is slowly absorbed by platinum, but iodine and bromine have no action upon it. A mixture of silica and carbon attacks platinum, and forms a siliciuret. Platinum crucibles are rapidly attacked when heated in a charcoal fire, inasmuch as the ashes always contain more or less silica. To preserve the platinum,

it is therefore indispensable to introduce it in a Hessian crucible, when it is to be heated with charcoal.

672. ALLOYS of platinum are formed with almost all the metals, at a temperature more or less elevated. In a state of subdivision it may be combined with mercury.

673. SPONGY PLATINUM. This metal presents itself under different aspects, according to the manner in which it has been produced. When it proceeds from the calcination of the ammoniacal chloride of platinum, it is spongy, tarnished, and of an ashy gray colour, and is called *spongy platinum*. In this state it acquires metallic lustre by friction.

674. PLATINUM BLACK. When platinum is precipitated from one of its solutions, it appears sometimes in the form of a black powder called *platinum black*.

This substance is prepared by different methods. Most commonly a solution of the bichloride, $PtCl_2$, is boiled with sugar, $C_{12}H_{11}O_{11}$, and carbonate of soda, NaO,CO_2, when the chloride of sodium, NaCl, is formed, metallic platinum precipitated, and the oxygen given up by the soda decomposes a part of the sugar, which is converted into water and carbonic acid. In this process it is necessary to shake the mattrass in which the mixture is contained from time to time, in order to prevent the precipitated platinum from adhering to its sides. The precipitate is, in fine, collected on a filter, and dried between folds of blotting-paper.

Liebig prepares platinum black, by dissolving the protochloride, PtCl, in a concentrated solution of potash, KO, and pouring alcohol $C_4H_6O_2$, little by little into the warm liquor, which is continually stirred until effervescence ceases. Carbonic acid is disengaged, and platinum is deposited as a black powder, which is then boiled successively with alcohol, hydrochloric acid, potash, and finally with water.

It may also be prepared by the decomposition of the sulphate of platinum by alcohol.

675. Platinum black has the property of condensing the gases in large quantities with a development of heat. When it has remained for some time in an atmosphere of oxygen, it will have absorbed several hundred times its volume of that gas, and will produce the phenomena of vivid combustion. Thus, if a drop of absolute alcohol be let fall upon it, inflammation will immediately ensue, and the platinum will become incandescent. If a capsule containing platinum black be placed under a receiver filled with atmospheric air, the sides of which are wetted with alcohol, the alcoholic vapour, $C_4H_6O_2$, will be slowly oxidated, and transformed into acetic acid, $C_4H_3O_3,HO$.

676. Platinum black, prepared by the different processes indicated above, does not possess this property in the same degree. That which is obtained by the decomposition of the sulphate of platinum by alcohol, is the most active.

677. SPONGY PLATINUM has the same property, but in an inferior degree. Thus, if a piece of spongy platinum be thrown into a re-

ceiver containing oxygen and hydrogen, in the proportions necessary to form water, explosion will immediately take place, the gases will combine, and the receiver will be filled with aqueous vapour, which will be condensed upon its surface. In the same manner, if a jet of hydrogen be projected on spongy platinum exposed in the air, the gas will be inflamed.

678. LAMINATED PLATINUM manifests this property only when heated to about 400°. If a spiral ribbon of the metal be suspended over the flame of a spirit-lamp, *fig.* 151, until it is raised to a red heat, and the lamp be then extinguished, the wire will continue incandescent for an indefinite time. The alcoholic vapour exhaled from the lamp-wick burns slowly in contact with the spiral ribbon of the metal, and in this combustion sufficient heat is developed to maintain the incandescence. This experiment will succeed better if a little ether be added to the alcohol to render it more volatile. The arrangement is generally known as *Davy's flameless lamp.*

Fig. 151.

The experiment may by varied thus. Let a little ether be poured into the bottom of a wine-glass, *fig.* 152, and let the spiral ribbon of platinum, previously rendered incandescent, and suspended from a card be let down into the glass, so that the card shall closely cover the mouth of the glass, while the spiral shall not touch the liquid ether. The spiral will continue incandescent as before.

Fig. 152.

In these and similar experiments the vapour of the alcohol and ether undergo only an incomplete combustion, producing volatile compounds of an acid and suffocating odour.

679. Nitric oxide, NO_2, and ammonia, NH_3, in an atmosphere of oxygen, are changed by contact with spongy platinum into nitric acid, NO_5. The compounds of nitrogen and oxygen in contact with spongy platinum in an atmosphere of hydrogen are, on the contrary, changed into ammonia.

$$NO_2 + 3O = NO_5, NH_3 + 5O = NO_5 + 3H, NO_2 + 3H = NH_3 + 2O.$$

To insure the success of these experiments, the platinum should be raised to 300° or 400° in a glass tube, through which the gaseous mixture should be transmitted.

680. Spongy platinum loses this property after a certain time, but it may be restored by heating it for a few seconds in nitric acid, and then calcining it at a dull red heat. Platinum black also loses this property, but recovers it if it be heated in nitric acid, and then washed with water and dried at a gentle heat. (Regnault.)

681. To reduce spongy platinum to the malleable state, it is introduced into a brass cylinder *e f g h*, *fig.* 153, to which a capsule of steel, *a b c d*, is fitted. A solid plunger of steel, *i k*, is fitted into the cylinder. When the cylinder is half filled with spongy platinum, the plunger is introduced, and submitted to the strokes of a hammer upon its upper extremity, at first gently, and afterwards with more force. The platinum is soon condensed, greatly reduced in volume, and in fine, converted into a pretty solid disc, which being raised to a white heat in a furnace, is hammered upon a steel anvil. By the frequent repetition

of these operations, a plate of the metal is obtained which is perfectly malleable, and which can be reduced to any degree of thinness by a rolling-machine.

682. THE OXIDES are, PtO and PtO_2.

683. THE PROTOXIDE, PtO, is only known as a hydrate, and is obtained by precipitating the protochloride of platinum by potash. It is deposited in the form of a black powder, a part of which remains in solution in the potash. It is very unstable, and when thrown upon burning charcoal is immediately reduced. It is dissolved slowly in nitric, sulphuric, and acetic acids, to which it imparts a brown colour. Boiling hydrochloric acid, resolves it into the bichloride and metallic platinum.

$$2HCl + 2PtO = PtCl + Pt + 2HO.$$

When recently precipitated, it is dissolved by potash and soda.

684. THE ANHYDROUS BINOXIDE, PtO_2, is black, its hydrate being a brownish yellow, resembling the hydrated protoxide of iron. It is completely decomposed by moderate heat, disengaging oxygen, and giving metallic platinum. Combustible bodies very easily reduce it. It is dissolved by the principal acids, forming salts of a brown colour. It combines with the alkalies, the earths, and metallic oxides, with which it plays the part of an acid, producing salts called *platinates*.

Fig. 153.

685. FULMINATING PLATINUM corresponds, probably, to fulminating gold and silver, but its composition has not yet been determined. It is pulverulent, of a dark brown colour, and does not detonate under the hammer, but at a temperature of about 400° it produces a strong detonation. It is insoluble in water and in nitric and chloric acids, but is dissolved by sulphuric acid.

It may be obtained by decomposing the ammoniacal chloride of platinum by potash, or precipitating the sulphate of platinum by ammonia and digesting the precipitate with an excess of ammonia.

686. THE SALTS of platinum have little importance, and have not yet been the subjects of much research.

Those of the protoxide form brown solutions. Potash does not precipitate them when their solutions are sufficiently dilute. Ammonia gives a green precipitate; carbonate of potash, a brown; and nitrate of the protoxide of mercury, hydrosulphuric acid, and hydrosulphuret of ammonia, a black. Carbonate of ammonia, the ferro- and ferrid-cyanide of potassium, give no precipitate. Iodide of potassium first produces a red and then a black precipitate.

The salts of the peroxide have an orange-yellow colour. Potash, ammonia, salts of potash and ammonia, and nitrate of the protoxide of mercury give yellow precipitates. Soda and its carbonate, ferro- and ferrid-cyanide of potassium, sulphate of protoxide of iron, and tannin give severally no precipitates.

The salts of platinum are all decomposed by heat, giving metallic platinum.

687. THE CHLORIDES, like the oxides, are the protochloride, PtCl, and the bichloride, $PtCl_2$.

688. THE PROTOCHLORIDE is greenish-brown, insoluble in water, and unalterable in the air. Exposed for a long time to light, its

surface is blackened. It is insoluble in nitric and sulphuric acids, but is sensibly dissolved by hydrochloric acid, being partly transformed into the bichloride, and metallic platinum. It is soluble, especially when heated, in a solution of the bichloride of platinum. Heat completely decomposes it. The alkalies form in its solution a precipitate of the hydrate of the protoxide of the platinum. It is easily combined with the chlorides of sodium, potassium, and with hydrochlorate of ammonia, forming compounds readily crystallisable.

It is prepared by dissolving platinum in aqua regia, evaporating the liquor to dryness, and heating the residuum carefully in an oil bath at about 400°, until it becomes insoluble in water.

689. THE BICHLORIDE is reddish-brown when in the solid state. Its solutions are dark yellow, its taste styptic, and its reaction acid. It is soluble in cold water, and gives by evaporation a deliquescent brown mass. It is very soluble in alcohol, and forms with hydrochloric acid a hydrochlorate of the chloride of platinum, which crystallises in cooling and loses its acid by continued evaporation. Heat changes it at first into the protochloride and then into metallic platinum. Sulphuric acid forms in its solution a yellow precipitate of the anhydrous bichloride. Mercury reduces it even in the cold.

It is prepared by dissolving platinum in aqua regia, consisting of two parts of hydrochloric and one of nitric acid, and evaporating the liquid to dryness to expel the excess of acid. It combines with almost all the chlorides, forming compounds, to which the name chloro-platinates has been given. Thus, the chloroplatinates of potash and ammonia are—

$$PtCl_2,KCl.$$

$$PtCl_2,NH_3,HCl.$$

690. THE SULPHURETS, like the oxides, are PtS and PtS_2.

691. THE PROTOSULPHURET is black, insoluble in water, and is obtained in the dry way by heating two parts of sulphur and one of finely divided platinum. It is produced in the humid way by the action of hydrosulphuric acid, or an alkaline sulphuret, upon protochloride of platinum.

692. THE BISULPHURET is obtained in the humid way by treating the chloride of platinum, or the double chloride of platinum and sodium, with hydrosulphuric acid or an alkaline sulphuret. This sulphuret is black. Heated in close vessels it gives up half its sulphur, and is transformed into the protosulphuret. Nitric acid affects it under the influence of heat, and changes it into the sulphate of the binoxide of platinum.

693. Two series of salts of platinum are formed by the combination of the protoxide and of the binoxide with the oxacids. The salts of the protoxide, formed with nitric and sulphuric acids, are not crystallisable. The nitrate of the binoxide has a dark brown colour. It is produced by treating the binoxide with nitric acid. The dilute solution of this salt has a pure yellow colour. The nitrate of the binoxide is produced when the auriferous alloys of platinum, rich in silver, are attacked by nitric acid.

Double salts are formed with nitrate of potash and soda.

694. ALLOYS OF PLATINUM are formed with a great number of metals. An alloy of platinum and potassium is obtained by heating these metals together. Iron combines with platinum in all proportions, forming alloys which can be flattened under the hammer, and are susceptible of a fine polish.

Copper and platinum easily combine. These alloys receive a fine polish, and are sometimes used for the specula of telescopes.

Lead combines with platinum, and consequently this metal must not be fused in a platinum crucible. Alloys of platinum with tin, zinc, bismuth, gold, &c., are known. Spongy platinum combines with mercury, but this metal has no action on forged platinum. Platinum and silver combine in all proportions; the silver renders the platinum completely soluble in nitric acid. A small proportion of platinum hardens silver.

695. METALLURGY OF PLATINUM. Platinum ore is found in the auriferous alluvial sands, and in certain localities with diamonds. The principal platinum mines are those of Choco in New Grenada, of Brazil, and of the Oural Mountains. Platinum ore consists of a mixture of platinum, iridium, osmium, palladium, iron, copper, and the osmide of iridium. It also contains iron in combination with chromium and titanium, and small spangles of the alloy of gold and silver, with a little mercury and sand.

The following analyses of some of the principal platinum ores have been given by Berzelius:—

	Nischne-Tagilsk. Siberia.		Gorobla-godat, Siberia.	South America.		
	Non-magnetic.	Magnetic.				
Platinum	78·94	73·58	86·50	84·30	86·06	84·34
Iridium	4·97	2·35	..	1·46	1·09	2·58
Rhodium	0·86	1·15	1·15	3·46	2·16	3·13
Osmium	..	..	..	1·03	0·97	0·19
Palladium	0·28	0·30	1·10	1·06	0·35	1·66
Iron	11·04	12·98	8·32	5·31	8·03	7·52
Copper	0·70	5·20	..	0·74	0·40	..
Osmide of Iridium and foreign matter	1·96	2·30	1·40	0·72	2·01	0·58

When platinum ore has been mechanically disembarrassed of the chief part of the foreign matter with which the metal is mixed, it is submitted several times successively to the action of a mixture of hydrochloric acid in excess and nitric acid, which effects the solution of the metal. This aqua regia is diluted with a small quantity of water, so as to dissolve as little as possible of the iridium, which renders the platinum brittle. The aqua regia is from time to time renewed, until the liquor ceases to be coloured yellow, when the platinum will be completely dissolved. It is necessary to conduct this process under a chimney having a strong draught, so as to carry off completely the nitrous and other noxious vapours which are disengaged. When the solution of platinum has been allowed to stand until it has become clear, it is decanted, and a concentrated solution of sal ammoniac is poured into it, which almost completely precipitates the platinum in the state of a double chloride of platinum and ammonia. Since, however, the mother waters still contain a

little platinum mixed with other metals, these are precipitated by slips of iron and zinc, when a black deposit is obtained, from which a certain quantity of platinum can be extracted. The deposit is for this purpose first treated with hydrochloric acid, which dissolves the foreign metals, and the residuum is then attacked by weak aqua regia, which easily dissolves the platinum, leaving the iridium almost untouched. Sal ammoniac is then poured in, which precipitates the double chloride of platinum and ammonia.

This double chloride calcined at a red heat, yields spongy platinum, which is reduced to powder by manipulation, and being mixed with water so as to form a sort of liquid mud, is spread upon a sieve through which the finer parts pass. The grosser parts remaining in the sieve are then again pulverised, avoiding however the use of any hard body, which would cause a partial aggregation. The greatest care and the most extreme neatness must be observed in all these operations; since a few grains of dust, or even a hair, in the turbid liquid from which the platinum is separated, would produce great defects in the metal. It is usual to wash the metallic dust several times with decantation, to divest it of all foreign matter.

The paste thus obtained is consolidated and rendered malleable by the apparatus shown in *fig.* 153, constructed on a large scale. The metal is compressed first with a wooden and afterwards with a metallic plunger. After a certain cohesion is imparted in this way to the metal, it is submitted to the action of an hydraulic press. The disc of metal resulting from these processes is raised to a white heat in an earthern crucible, placed on an anvil, and submitted to the strokes of a heavy sledge hammer. It is then again heated, and finally forged.

ORGANIC CHEMISTRY.

CHAPTER XVIII.

COMPOSITION OF ORGANIC BODIES.—IMMEDIATE AND ELEMENTARY ANALYSIS.

696. ORGANIC nature, notwithstanding its surprising variety and beauty, is formed almost exclusively of four elements, carbon, hydrogen, oxygen, and nitrogen. The other metalloids enter into the composition of organic bodies comparatively seldom, many not at all. Few of the metals are admitted, and these few in rare cases.

Although organised bodies are thus simple in their composition, so far as relates to the variety of the materials of which they are formed, they are incomparably more complex than inorganic compounds, so far as relates to the number of equivalents of their constituents. Thus, while the number of equivalents of the simple constituents of inorganic compounds is generally limited to 3, and almost never exceeds 5, that of the constituents of organic compounds generally exceeds 10, and often amounts to from 50 to 100. This remarkable difference in the constitution of the two classes of natural compounds will be rendered conspicuous as the student proceeds.

697. Inorganic bodies are, for the most part, capable at once of analysis and synthesis, of decomposition and recomposition. The chemist can generally solve the problem, "given the components, to produce the compound," as well as, "given the compound, to exhibit the components." But in the case of organic bodies it is quite otherwise. Analysis is generally practicable; but synthesis, save in the most rare and exceptional instances, cannot be effected. Sugar can be resolved into 12 equivalents of carbon, 11 of hydrogen, and as many of oxygen; but by no known process can these elements be converted into sugar.

698. With occasional exceptions, identity of constituents infers identity of character and properties, in the case of inorganic bodies. If 2 bodies are known to consist of 8 parts, by weight, of oxygen and 1 of hydrogen, it may be certainly inferred that both are water, no other body having the same composition. But this is not at all the case with organic bodies. Identity of composition not only does not infer identity of properties, but does not even supply ground for a presumption of such identity. *Isomerism* here loses the character of an exception, and almost

assumes that of a rule. Sugar and gum arabic are identical in composition. So are the very different oils of turpentine, juniper, lemons, copaiva, pepper, and cubebs. The difference of character and properties thus manifested by bodies identical in chemical composition must be ascribed to different modes of action of the vital force, under the influence of which such compounds have been formed.

699. A compound may be resolved by analysis, either into its more immediate components, or into its ultimate and elementary constituents. Thus, a salt may be resolved into the acid and the base of which it is immediately formed, or it may be resolved into its ultimate elements, the metalloid of the acid, the metal of the base, and the oxygen of the one and the other. The former process is denominated *immediate*, and the latter *elementary* or *ultimate* analysis.

Since organised nature is formed out of the elements of the inorganic world, the ultimate constituents of all organic compounds must be the inorganic elements.

700. THE IMMEDIATE ANALYSIS of organic bodies is one of the most difficult classes of problems presented in the laboratory. This is owing to the facility with which the immediate components yield to decomposition. Whatever be the agents, whether physical or chemical, applied to resolve the compound, they will be liable also to resolve the components; so that the analysis, instead of being immediate, will be elementary.

701. Organic components may often be separated by distillation; but, in resorting to this process, care must be taken that the temperature be not so high as to decompose the components.

702. When several components of the same substances are unequally volatile, they may be isolated by a succession of distillations at graduated temperatures. In such processes the practical difficulties are so much the greater the nearer to each other are the boiling points of the matters to be distilled.

703. The immediate analysis of the extensive class of organic compounds, whose only constituents are carbon and hydrogen, or these combined with oxygen, is effected by placing the compound in the presence of oxygen, under such conditions as will cause that gas to enter into combination with the carbon and hydrogen, so as to form carbonic acid and water, which, being accurately weighed, the quantity of carbon contained in the one and of hydrogen in the other, will give those two constituents of the compound under analysis, and the remainder, if any there be, will be the oxygen.

704. NITROGENISED COMPOUNDS cannot be analysed by the process explained above without some essential modifications. If nitrogen enter as a constituent, its presence may be easily mani-

fested by heating a small portion of the compound with solid hydrate of potash in a test tube, when the water of the hydrate will give up its hydrogen to the nitrogen to form ammonia, NH_3, which will be recognised by its characteristic odour, as well as by its alkaline reaction.

CHAPTER XIX.

ORGANIC ACIDS IN GENERAL.

705. ORGANIC bodies in general may be conveniently grouped in 3 classes: 1°. Acids; 2°. Bases; 3°. Neutrals.

Before stating the special qualities of the most important of the acids, it will be necessary to explain some properties and characters which are common to them, and also to notice a class of compounds called *amides*, derived from them by the action of ammonia.

706. Acids constitute the most numerous and important of the organic compounds. Although they present a close analogy to the mineral acids, in respect of their strength, their reactions, the affinities in virtue of which they form salts, and some other qualities physical and chemical, they offer in general no analogy at all in their composition, not being binary compounds of a radical with either oxygen or hydrogen.

M. Liebig has recently shown that in general they present a remarkable analogy to phosphoric acid. Professor Graham has shown that this acid has three definite hydrates, including 1, 2, and 3 equivalents of water respectively, and that these require 1, 2, and 3 equivalents of bases to produce neutral salts, these salts being denominated accordingly *mono-*, *bi-*, and *tri-basic*, § 179. A general examination of the organic acids and their salts has led to the discovery that they, like phosphoric acid, form salts which are *mono-*, *bi-*, or *tri-basic*. It is by the study of their salts, therefore, that the classes of the organic acids are determined.

707. Those organic acids which do not contain nitrogen are, with some exceptions, colourless, solid, and crystallisable.

Among the exceptions are a few brown acids, some resinous compounds, and liquid acids, such as formic, acetic, butyric, valerianic, caproic, and capric.

708. Acids having a heavy equivalent are either very sparingly soluble, or altogether insoluble in water, such as the fat acids and the resins. Those, on the contrary, which have a light equivalent are almost always soluble, such as acetic, formic, tartaric, citric, lactic, and malic acids.

709. Those acids which are capable of being volatilised without

change are mostly monobasic; but this statement is not convertible, since many monobasic acids are decomposed by heat, as are many of the polybasic.

710. The volatile acids contain not less than 3 equivalents of oxygen when in combination, that being the state in which they are anhydrous.

711. When polybasic acids are decomposed by heat, they generally evolve two or more equivalents of water or carbonic acid, and are reduced to other acids, called from the process *pyrogenous.*

712. EXAMPLES:—

$$\underbrace{C_8H_4O_8,2HO}_{\text{Malic.}} = \underbrace{C_8H_2O_6}_{\text{Maleic.}},2HO + 2HO.$$

$$\underbrace{C_{12}H_6O_{14},2HO}_{\text{Mucic.}} = \underbrace{C_{10}H_3O_5,HO}_{\text{Pyromucic.}} + 6HO + 2CO_2.$$

In these cases the maleic and pyromucic are pyrogenous acids.

713. It sometimes happens that by the application of heat the acid is rendered completely anhydrous; but, the pyrogenous acids once obtained, the original acids from which they were derived cannot be reproduced by combination with water or carbonic acid by any known physical or chemical agency. It would appear that such compounds can only be formed under the influence of vital force.

714. It seems also that the affinity of the acids for bases is essentially dependent upon the water they include; for, when rendered anhydrous, they are not only indifferent to the bases, but have no reaction on litmus, and, when put in presence of ammonia, produce the class of compounds called *amides.*

715. The anhydrous acids may be hydrated, either by long-continued contact with water at common temperatures, or by the effect of ebullition; but in thus taking up water they do not always resume their full complement of equivalents of it, but, on the contrary, sometimes form a series of inferior hydrates, which constitute so many peculiar acids, each having peculiar capacities of saturation, resembling the characters of phosphoric acid already noticed. Anhydrous *tartaric* and *paratartaric* acids present remarkable examples of this. (Frémy.)

716. Chlorine attacks certain organic acids, producing other acid compounds. Thus, according to Dumas, it changes acetic, $C_4H_3O_3,HO$, into *chloracetic acid*, $C_4Cl_3O_3,HO$.

717. Nitric acid decomposes most of the organic acids, producing water, carbonic acid, more highly oxygenated acids, and generally oxalic acid. In many cases nitrogenised acids result from the reaction.

718. The hydrate of potash in fusion transforms several organic compounds into acetic and oxalic acids, sometimes disengaging hydrogen. The following are examples :—

$$\underbrace{C_8H_4O_{10}}_{\text{Tartaric.}},2HO = 2\underbrace{(C_2O_3,HO)}_{\text{Oxalic.}} + \underbrace{C_4H_3O_3,HO}_{\text{Acetic.}}.$$

$$\underbrace{C_{12}H_5O_{11}}_{\text{Citric.}},3HO + 2HO = 2(C_2O_3,HO) + 2(C_4H_3O_3,HO).$$

$$\underbrace{C_{12}H_8O_{14}}_{\text{Mucic.}},2HO = 2(C_2O_3,HO) + 2(C_4H_3O_3,HO).$$

The volatile acids are generally decomposed into very distinct constituents by distillation with lime or baryta, the elements of carbonic acid remaining in combination with these bases, and carburets of hydrogen, oxygenated essences, and a class of compounds called *acetones* being disengaged.

719. ACETONES are compounds which result from the distillation of certain organic salts of lime, such as the benzoates, valerates, butyrates, margarates, stearates, and so on, and which differ from the acid constituent of the salt by 1 equivalent of carbonic acid. The name *acetone*, originally applied to pyroacetic spirit, produced by depriving acetic acid of 1 equivalent of carbonic acid, has thus been generalised.

720. Sulphuric acid heated with organic acids often decomposes them, seizing on a part of their water, but sometimes combines with them to form a double acid.

Distilled with phosphoric acid the organic acids are sometimes dehydrated and converted into carburets of hydrogen.

721. THE PREPARATION OF ORGANIC ACIDS is generally made by the common oxidising reagents, such as nitric, chromic, and plumbic acids, the mixture of sulphuric acid with the peroxide of manganese, the hydrate of potash, and aqueous solution of chlorine.

It is by the agency of concentrated nitric acid, and a mixture of sulphuric acid and peroxide of manganese, that oxalic and formic acids are produced, which represent the last terms of oxidation of organic molecules. When it is desired to produce less degrees of oxidation, plumbic and dilute nitric acids are used.

The hydrate of potash may be considered as a feebly oxidating reagent, producing acids closely related in composition to the bodies from which they are derived. Thus, it oxidises a great number of essential oils, without burning their carbon, and forms benzoic, cinnamic, valerianic, cuminic, and other analogous acids.

Aqueous solutions of potash are used to produce acids derived from organic compounds, either by oxidation or decomposition. It is thus that the fat acids are produced by the decomposition of neutral fat bodies under the influence of the alkalies.

The alcohols may be immediately oxidised by free oxygen in the presence of platinum black, producing a certain number of organic acids. Acetic, formic, valerianic, and some other acids may be obtained in this manner.

Ferments also produce organic acids, such as acetic, lactic, tannic, pectic, butyric.

Organic acids also result from the agency of heat. The pyrogenous acids obtained in this way have been already mentioned. Acetic acid is produced by the distillation of almost all neutral bodies, and of several organic acids.

Nitrogenised acids are produced by various methods, such as the action of nitric or a mixture of nitric and sulphuric acids, or ammonia, on organic bodies, or by the action of potash on certain neutral nitrogenised bodies. The acids resulting from these different processes differ generally in their properties. Those obtained by nitric acid are often yellow, and form with bases salts which detonate or fuse when heated, and are thus related to the nitrates. When their salts are heated with a mixture of sulphuric acid and peroxide of manganese, nitrous vapours are disengaged.

722. AMIDES are a class of compounds, the type of which was discovered in 1830 by Dumas, in experiments upon the distillation of the oxalate of ammonia. The neutral oxalate of ammonia, NH_3,HO,C_2O_3, being submitted to distillation in a small glass retort, parts with the elements of 2 equivalents of water, the compound remaining being *oxamide*.

$$\underbrace{NH_3,HO,C_2O_3}_{\text{Oxalate of ammonia.}} = \underbrace{C_2O_2,NH_2}_{\text{Oxamide.}} + 2HO.$$

Dumas, anticipating the discovery of a class of analogous compounds, gave the name *amides* to every neutral nitrogenised body which differs from an ammoniacal salt by the elements of water, and which regenerates the salt when submitted to influences by which water can be recombined with it. This anticipation has been fully realised by succeeding discoveries.

723. It appears from what has been explained above, that the organic acids are an exceedingly numerous class of compounds, since there is scarcely an organic body which does not produce one or several when submitted to various physical and chemical agencies. Since it would be impossible within the limits of this compendium to give even the shortest notice of each of them, we shall briefly explain the characters and leading properties of the most important.

CHAPTER XX.

THE PRINCIPAL ORGANIC ACIDS.

724. OXALIC ACID, C_2O_3,HO, may be regarded as a hydrated sesquioxide of carbon. It is found in a great number of plants, like sorrel, to which it imparts a sour taste. It is extracted from a sort of dockweed (Rumex) in the Black Forest, by pounding the plant in troughs, and expressing the juice. The liquor, after being clarified, is evaporated to crystallisation. The crystals thus obtained

are the oxalate of potash, known in commerce as *salt of sorrel*. To extract the oxalic acid, acetate of lead is poured into a solution of the salt of sorrel, when double decomposition takes place, oxalate of lead being precipitated. This latter salt is decomposed by sulphuric acid, and crystals of oxalic acid, C_2O_3,HO, are obtained by evaporation.

725. OXAMIDE, which as already stated is the type of the entire class of amides, can be obtained from oxalate of ammonia only in very small quantities. It may be prepared pure and more abundantly, according to Liebig, by mixing oxalic ether with an excess of liquid ammonia. After a short interval the oxamide is deposited in the form of a white crystalline powder, which may be filtered, washed with distilled water, and dried at a low temperature. The reaction may be thus expressed :—

$$\overbrace{C_2O_3,C_4H_5O}^{\text{Oxalic ether.}} + \overbrace{NH_3}^{\text{Ammonia.}} = \overbrace{C_2O_2,NH_2}^{\text{Oxamide.}} + \overbrace{C_4H_5O,HO}^{\text{Alcohol.}}.$$

Oxamide is white, tasteless, odourless, and without action on the test papers. Although volatile, it suffers partial decomposition by heat. Boiling water dissolves it sparingly, and deposits it on cooling in white flakes. It is not sensibly soluble in alcohol. One of its characters is the facility with which it is converted into oxalate of ammonia by combination with the elements of water. This change may be directly made with water alone in a digester at 255°.

726. OXAMIC ACID, C_4O_5,NH_2,HO, is obtained by distilling the bi-oxalate of ammonia, $NH_3,HO,(C_2O_3)_2,HO$, in an oil bath at 446°. This salt loses first its water of crystallisation, then disengages carbonic acid and carbonic oxide, and next carbonate and hydrocyanate of ammonia; and, if the distillation be not pushed too far, the residuum will consist almost exclusively of oxamide and oxamic acid, the latter of which may be obtained in the form of a yellowish powder by heating the acid liquor with concentrated solutions of the salts of baryta or lime, precipitating the oxamates, from which oxamic acid may be obtained in solution by sulphuric acid. The solution being evaporated, the oxamic acid in powder will remain.

Oxamic acid is decomposed by heat, disengaging water, carbonic acid, and carbonic oxide, and leaving oxamide.

$$\overbrace{C_4O_5NH_2,HO}^{\text{Oxamic acid.}} = HO + CO + CO + \overbrace{C_2O_2NH_2}^{\text{Oxamide.}}.$$

727. ACETIC ACID, $C_4H_3O_3,HO$, which is the sour principle of common vinegar, is formed when alcohol is submitted, under suitable conditions, to the action of oxygen. Thus—

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}} + 4O = \overbrace{C_4H_3O_3,HO}^{\text{Acetic acid.}} + 2HO;$$

the result being acetic acid, diluted with 2 equivalents of water.

This may be demonstrated directly by putting alcohol, under certain conditions, in contact with oxygen or with atmospheric air.

Let a small capsule containing platinum black be put upon a plate, *a*, *fig.* 154, and covered by a tubulated receiver, resting on three pieces of cork, so as to allow free circulation of air between the receiver and the plate; and let a glass funnel, with a long narrow neck brought to a fine point, be inserted in the tubulated opening at the top, so as to allow free circulation of air between it and the receiver. Let this funnel be filled with alcohol, which will fall slowly drop by drop upon the platinum. An elevation of temperature and the development of vapour will ensue. This vapour will be condensed upon, and will trickle down the inside surface of the receiver, and will collect in a liquid state upon the plate. This liquid will be acetic acid, nearly pure.

In this case the platinum, without intervening directly in the reaction, excites by its presence the affinities, and promotes the combination by exposing a large surface of the spirit to the oxygen of the air.

Fig. 154.

Fig. 155.

728. Certain nitrogenised substances exercise an influence analogous to that of the platinum in this case, and it is to their presence that many familiar cases of acetification must be ascribed. Thus wine holds in solution a nitrogenous principle, which causes its alcohol to absorb the proportion of oxygen necessary to convert it into acetic acid. Hence the production of wine vinegar. In general, in the fabrication of wine vinegar, however, various organic compounds are used to promote the change, the chief of which is a gelatinous substance, deposited in the casks in which the vinous fermentation has taken place, called *mother of vinegar*.

The acidification of wine may be prevented, either by preserving it from contact with oxygen, or by precipitating the nitrogenous matter, by the presence of which the oxigenation of its alcohol is promoted.

729. All the conditions favourable to acetification are united in the method of Schurenbach for the fabrication of vinegar.

Dilute alcohol is poured several times upon beech-wood shavings, mixed with the must of beer, and placed in a barrel, A, *fig.* 155, pierced laterally with a row of holes, *a*, *a*, *a*. Alcohol of 80 per cent. strength, mixed with 6 times its weight of water, is poured 3 or 4 times successively into the barrel, and received in a small vessel, B. The process is usually finished in about 36 hours. The acetification is more rapid when the shavings have been previously sprinkled with strong vinegar.

The wood shavings are intended to increase the surface of the liquid exposed to the contact of air, but independently of this they contain nitrogenised

matter, which promotes the oxigenation of the alcohol. The must of beer also stimulates the acetification. Heat is developed in the process sufficient to raise the temperature of the mass to 104°.

730. Starch can be converted into sugar under the influence of nitrogenised bodies or acids, and from this sugar alcohol is produced, which is used for the manufacture of the inferior sorts of vinegar. 4·5 grains weight of barm and 440 grains of starch, dissolved in a quart of water, will produce vinegar in a week. 124 parts of sugar, 80 of beer barm, and 868 of water, exposed in a warm place for about a month, will be converted into vinegar of good quality.

731. PYROLIGNEOUS ACID is the name given in commerce to an impure solution of acetic acid, produced by the distillation of wood.

This process is executed in large cylindrical vessels made of sheet iron, riveted like steam-boilers. These cylinders are connected by pipes with condensers. The gases evolved in the process are conveyed in tubes to the furnace which maintains the distillation.

The result of the condensation is a liquid, consisting of water, tar, wood-spirit, acetate of methylene, and acetic acid. The tar, which floats, is skimmed off, and the liquid is passed into a copper still. The first product of the distillation is wood spirit, and this is succeeded by the liquid known as *pyroligneous acid.*

This acid is always coloured, and has a tarry savour, of which it cannot be divested by mere distillation. It can only be removed by causing it to enter into combination with a base, when the tar can be separated without affecting the acetate.

732. Acetic acid below 63° is solid, above this temperature it is a colourless liquid, SG = 1·063. Its odour is characteristic, and its taste pungent. It is nearly as corrosive as the strongest mineral acids. It boils at 248°. Its vapour is inflammable, burning with a blue flame. The density of the vapour at 306° is 2·78, which corresponds to 3 volumes. At 446° the density is 2·09, which corresponds to 4 volumes.

Acetic is distinguished from some other vegetable acids by dissolving fibrine, and not precipitating albumen.

733. ACETONE, or PYRO-ACETIC SPIRIT, $C_6H_6O_2$, is produced by decomposing acetic acid by heat. This is effected by transmitting the vapour of the acid through a porcelain tube at a dull red heat, 2 equivalents of water and 2 of carbonic acid being disengaged :—

$$2(C_4H_3O_3,HO) = C_6H_6O_2 + 2HO + 2CO_2.$$

At a still more elevated temperature the acid is completely decomposed, being resolved into carbon and inflammable gases. Acetone is also produced by the distillation of the acetates. Thus acetate of lime is resolved into the carbonate and acetone :—

$$2(CaO,C_4H_3O_3) = 2(CaO,CO_2) + C_6H_6O_2.$$

Pure acetone is limpid and transparent, with a penetrating odour and taste. It boils at 133°. Its SG = 0·7921, that of its vapour

being 2·022. It is soluble in all proportions in water, alcohol, and ether.

According to Sir R. Kane, acetone may be considered as the hydrated oxide of an hypothetic compound radical, C_6H_5, which he calls *mesityle*. This view, though supported by some analogies, has not been generally assented to by chemists. The true hydrated oxide of the body, C_6H_5, has been lately discovered by Hofmann, and was obtained from *glycerine*; §§ 903, 913.

734. SULPH-ACETIC ACID, $C_4H_2O_2,(SO_3)_2$, 2HO, is produced by the reaction of anhydrous sulphuric on acetic acid, by which the latter loses 2 equivalents of water.

The composition of the sulph-acetates is $2(MO), C_4H_2O_2, (SO_3)_2$.

735. CHLOR-ACETIC ACID, $C_4Cl_3O_3,HO$, is obtained by the direct action of chlorine on acetic acid, under the influence of solar radiation. Chlorine replaces hydrogen, equivalent for equivalent.

736. THE ACETATES, when neutral, are represented by the general formula $MO,C_4H_3O_3$, acetic acid being monobasic. These salts are all decomposed by heat. Some of them, those of silver and copper for example, give highly concentrated acetic acid by distillation, with a metallic residuum, the oxygen of the oxide thus decomposed burning a part of the acid.

Acetates easily decomposed by heat, having a base which has a stable carbonate, yield acetone by distillation. Thus the acetate of baryta gives—

$$2(BaO,C_4H_3O_3) = 2(BaO,CO_2) + C_6H_6O_2.$$

All the acetates are soluble in water, the least so being those of molybdenum, tungsten, silver, and protoxide of mercury. These salts are generally decomposed by the stable acids, the disengagement of acetic acid being perceivable by the odour of vinegar thus produced.

737. THE NEUTRAL ACETATE OF POTASH, $KO, C_4H_3O_3$, may be prepared by the reaction of acetic acid on carbonate of potash, KO, CO_2. This salt, formerly called *foliated earth of tartar*, exists in abundance in the sap of plants, producing by their calcination the chief part of the carbonate of potash found in the ashes. It is white, very soluble in water, and deliquescent. Its solution in alcohol is decomposed by carbonic acid, which precipitates carbonate of potash, and sets free the acetic acid. Heated with an excess of potash it is transformed into the carbonate and light carburetted hydrogen :—

$$KO,C_4H_3O_3 + KO,HO = 2(KO,CO_2) + C_2H_4.$$

This reaction supplies the best method of preparing protocarburetted hydrogen.

738. ACETATE OF SODA, $NaO, C_4H_3O_3$, formerly known as *foliated mineral earth*, is prepared by the direct reaction of acetic acid on carbonate of soda. It is also obtained by the action of

sulphate of soda on acetate of lime. If concentrated solutions of sulphate of soda and acetate of lime be mixed, a double sulphate of lime and soda will be precipitated.

It crystallises in oblique prisms, with a rhomboidal base, and contains 6 equivalents of water.

739. ACETATE OF AMMONIA, employed in medicine under the name of *spirit of Mindererus*, is produced by the immediate reaction of the acid on the alkali. One of its properties is to arrest intoxication.

740. ACETATES OF LIME AND BARYTA are soluble in water, and crystallisable and easily decomposed by heat, being resolved into the carbonate and acetone.

ACETATE OF ALUMINA, $Al_2O_3,3(C_4H_3O_3)$, is prepared by precipitating sulphate of alumina by acetate of lead. It is very soluble in water, but not crystallisable.

This salt has great commercial importance, owing to its application as a *mordant* in calico-printing. Gay Lussac observed that a solution boiled in the presence of sulphate of potash, alum, or sea salt, becomes turbid when warm, and clear when cold, from which the calico printer has learned that the mordant should not be used hot. When cold, the colours are fresher and more vivid.

741. ACETATES OF THE PROTOXIDE AND PEROXIDE OF IRON are obtained mixed, by the direct action of the acid on the metal. They are known in commerce as the *pyrolignite of iron*, *iron liquor*, or *black broth*. The acetate of the peroxide is employed in dying black. Not containing an excess of acid, it does not injure the quality of the cloth.

742. THE ACETATES OF LEAD are four: 1°. neutral, $PbO, C_4H_3O_3$; 2°. sesquibasic, $(PbO)_3, (C_4H_3O_3)_2$; 3°. tribasic, $(PbO)_3, C_4H_3O_3$; and, 4°. sexbasic $(PbO)_6, C_4H_3O_3$: of these the last three are called *subacetates*, the proportion of the acid to the basic element being less than in the neutral salt.

The neutral acetate is prepared either by the direct reaction of the acid on litharge, or by exposing a mixture of the acid and the metal in the air, when the metal is oxidised and the acid combines with the oxide.

This salt, commonly known as *sugar of lead*, and sometimes called *salt of latron*, crystallises in right rhomboidal prisms, with dihedral summits. It effloresces in air, and can be rendered anhydrous by desiccation. When cautiously heated it dismisses a part of its acid, and is reduced to the sesquibasic salt. It is soluble in the cold, in 1·5 parts of water and 8 of alcohol. A solution of it poured cold into an excess of ammonia, throws down the sexbasic salt as a white insoluble precipitate.

The solution of the bibasic salt in water, is the liquid known in medicine as *Goulard water*.

743. THE ACETATES OF COPPER are: 1°. neutral, CuO, $C_4H_3O_3$; 2°. sesquibasic, $(CuO)_3$, $(C_4HO_3)_2$; 3°. bibasic, $(CuO)_2$, C_4HO_3; and, 4°. tribasic, $(CuO)_3$, $C_4H_3O_3$.

The neutral acetate, sometimes called *distilled vert-de-gris*, is prepared by dissolving vert-de-gris in acetic acid. It is soluble in water, and crystallises in rhomboidal prisms, containing one equivalent of water. It is efflorescent, and but slightly soluble in alcohol. Like all the soluble salts of copper, it is poisonous. It is resolved by heat into highly concentrated acetic acid, acetone, a small quantity of gas, and metallic copper.

This salt is employed in dyeing wool black.

The bibasic acetate is vert-de-gris, which, however, should not be confounded with the greenish salts formed where copper in contact with fatty matter, is exposed to the air. This salt is obtained by spreading the residuum of pressed grapes on sheets of copper. The alcohol contained in this residuum is acidified, and the acetic acid resulting forms the acetate with the copper oxidised by the air.

744. KAKODYL OR CACODYLE, C_4H_6As, is a compound base, discovered by Bunsen, and is a constituent of an extensive class of compounds. Its protoxide, C_4H_6AsO, has been long known as the *fuming liquor of Cadet*. The base kakodyl, has been isolated by Bunsen, and shown to have a system of reactions analogous to those of the metals.

745. The oxide is prepared by the distillation of a mixture of equal weights of arsenious acid and acetate of potash, carbonic acid and carbonate of potash being separated :—

$$\underbrace{2(KO,C_4H_3O_3)}_{\text{Acetate of potash.}} + \underbrace{AsO_3}_{\text{Arsenious acid.}} = 2CO_2 + 2(KO,CO_2) + \underbrace{C_4H_6AsO}_{\text{Oxide of kakodyl.}}$$

Oxide of kakodyl is a colourless ethereal liquid, of high refracting power. It boils at 302°, and congeals at 9° into a white crystalline mass. The SG of its vapour is 7·6. Its odour is alliaceous, resembling that of arseniuretted hydrogen. It produces painful itching of the skin, and taken internally acts as a strong poison.

Exposed to the air it burns spontaneously with a white flame. It is insoluble in water; dissolves phosphorus, sulphur, and iodine; and burns in chlorine. The acids easily dissolve it, producing crystallisable salts.

746. FORMIC ACID, C_2HO_3,HO, which derives its name from being secreted by a species of ant (*formica*), results from the action of almost all strong oxidants on organic matter.

This monohydrated acid is liquid at common temperatures, fumes in air, crystallises below 32° in brilliant micaceous plates, and boils at 32°. Its SG = 1·235. Its vapour is inflammable, burning with a blue flame. Combined with water, it forms two definite hydrates, and has not been dehydrated. It loses its water only when it combines with bases to form formiates.

It is one of the most corrosive acids. It acts on the animal economy like nitric acid. Sulphuric acid decomposes it, resolving it into water and carbonic oxide :—

$$C_2HO_3,HO + SO_3,HO = 2(CO) + SO_3,HO + 2HO.$$

Oxidants transform it into carbonic acid and water :—

$$C_2HO_3,HO + 2O = 2(CO_2) + 2HO;$$

a reaction which characterises formic acid.

747. TARTARIC ACID, $C_8H_4O_{10}$, 2HO, is found in abundance in the fruits, leaves, and roots of plants. It is prepared by decomposing tartrate of potash, KO, HO, $C_8H_4O_{10}$, commonly known as *cream of tartar*, by carbonate of lime.

This acid crystallises in oblique rhomboidal prisms, with dihedral summits, which are unalterable in the air. It has an agreeable acid taste, is soluble in 1·5 parts of cold, and in a much less proportion of boiling water. It is soluble also in alcohol and wood spirit, and presents in contact with these two liquids phenomena of much interest.

At 300° it is resolved into acetic and oxalic acids :—

$$\underbrace{C_8H_4O_{10},2HO}_{\text{Tartaric.}} = \underbrace{C_4H_3O_3,HO}_{\text{Acetic.}} + 2\underbrace{(C_2O_3,HO)}_{\text{Oxalic.}}$$

Oxidants easily decompose it, resolving it into carbonic and formic acids.

Tartaric acid with bicarbonate of soda forms the ordinary effervescent draughts.

748. THE TARTRATES constitute an important series of compounds. They may be grouped in three classes :—

1°. Tartrates in which two equivalents of the same base neutralise the acid, as for example, the neutral tartrate of potash, 2KO, $\overline{T}$, the acid being expressed by $\overline{T}$.

2°. Tartrates in which the acid is neutralised by single equivalents of two different bases, as for example, the neutral tartrate of potash and soda, KO, NaO, $\overline{T}$.

3°. Tartrates in which the acid is imperfectly neutralised by a single equivalent of a base, and a single equivalent of water, as for example, the acid tartrate of potash, KO, HO, $\overline{T}$.

749. CREAM OF TARTAR, KO, HO, $C_8H_4O_{10}$, the most important of the tartrates, exists in the juices of many fruits and vegetables, but especially in those of the grape and tamarind. It is more abundant in green than in ripe grapes, and in bad than good ones. It is always accompanied by the tartrate of lime. It is deposited in a thick crystalline crust, called *raw tartar*, on wine casks. In this state, however, it always requires purification.

This salt crystallises in oblique rhomboidal prisms, which crack between the teeth, have an acid taste, and redden litmus. When heated it has an agreeable odour of caramel. It is sparingly soluble in water, 184 parts of water being necessary for the solution of 1 part of the salt. It is insoluble in alcohol. When

calcined, it leaves a residuum called *black flux*, which is in fact an intimate mixture of carbon with carbonate of potash.

If cream of tartar be calcined with two parts of nitre, the carbon of the organic matter is altogether burnt, and the residuum is called *white flux*.

This salt is used as a mordant.

750. THE TARTRATE OF POTASH AND SODA is commonly known as ROCHELLE SALTS. This salt is prepared by neutralising a hot solution of cream of tartar with carbonate of soda, and crystallising by evaporation. It has a mild saline taste, and is used as an aperient.

751. THE TARTRATE OF POTASH AND ANTIMONY is the salt commonly known as *tartar emetic*. It is prepared by boiling teroxide of antimony in a solution of cream of tartar. It has a disagreeable metallic taste, provokes vomiting (from which it takes its name), and is poisonous. Dried at 212°, it parts with its water of crystallisation, and becomes anhydrous.

752. CITRIC ACID, $C_{12} H_5 O_{11}$, 3HO, is the principle which imparts the characteristic acid taste to lemon juice, from which its name is taken. It also exists in the juice of many other fruits, such as the orange, the tamarind, the gooseberry, currant, strawberry, &c. It is found in these juices sometimes free, and sometimes as an acid citrate.

Citric is a tribasic acid, in which one or more equivalents of water are interchangeable with the metallic bases, so that the citrates in general are represented by the three formula, (MO), $(HO)_2, \overline{C}$; $(MO)_2, (HO), \overline{C}$; and $(MO)_3, \overline{C}$; the acid being expressed by $\overline{C}$.

It is soluble in water, crystallises in rhomboidal prisms, and has an agreeable taste. It is distinguished from tartaric acid (with which, in commerce, it is sometimes adulterated) by not precipitating lime water, except when the liquor boils. It is very soluble in water and alcohol, but quite insoluble in ether. Exposed in the air it is soon covered with mouldiness. A like effect is produced on tartaric acid.

Nitric acid heated with citric acid, transforms it into oxalic acid.

Citric acid is employed in the preparation of lemonades. A lemonade consisting of a solution of citrate of magnesia, is an agreeable and efficacious laxative. Citric like oxalic acid effaces iron moulds. It is used to precipitate safflower, and for certain delicate processes in dyeing.

753. MALIC ACID, $C_8 H_4 O_8$, 2HO, abounds in the vegetable kingdom, either free or combined with bases. It exists in apples (from which it derives its name), pears, green plums, green gooseberries, elder and service berries, the pulp of the tamarind, barberry, pine-apple, tobacco, spinach, and numerous other plants and fruits.

In combining with bases, two equivalents of the base replace the two equivalents of water which it contains in the free state. It is therefore considered as *bibasic*.

754. *Maleic acid* is found in several vegetables, and especially in the *Equisetum*

fluviale, from whence it has been also called *equisetic acid*. It is changed into paramaleic acid by maintaining it for some time at the temperature of 300°.

These isomeric acids have different properties. Maleic is very soluble in water, paramaleic sparingly so. The latter forms with oxide of silver, a remarkable insoluble salt. It is found in several vegetables, especially the *fumitory*, and has thence been called *fumaric acid*.

755. LACTIC ACID prevails in the animal organism, being found in milk (from which it takes its name), blood, urine, the muscles, &c. It has been lately traced in the gastric juice. It also exists in almost every vegetable juice submitted to fermentation, the particular condition under which it is produced, being called *lactic fermentation*.

This acid is liquid, colourless, tasteless, uncrystallisable, and of a syrupy consistence. It is soluble in all proportions in water, alcohol, and ether. Its taste is acid and agreeable; poured in small quantity into milk, it produces coagulation. Curdled milk is consequently always acid.

It dissolves phosphate of lime readily, and in virtue of this property has been applied for the dissolution of stone in the bladder.

756. *Lactone*, $C_{10} H_8 O_4$, a liquid substance of pungent odour, which is to lactic acid what acetone is to acetic acid, is produced in the decomposition of lactic acid by heat.

757. LACTATES are very various, some being basic, others neutral, bibasic, or bisalts. Those best known are neutral salts, the composition of which is MO, $C_6 H_5 O_5$. Most of these are soluble and crystallisable. With the exception of the lactate of nickel, they lose their water of crystallisation at 212°.

758. TANNINS are a class of peculiar astringent substances, derived from various vegetable bodies, such as nutgalls, the bark of oak, Indian chestnut, elm, willow, and various others.

They are generally feeble acid compounds, the most important being those obtained from oak bark and nutgalls, to which all the rest bear a close analogy.

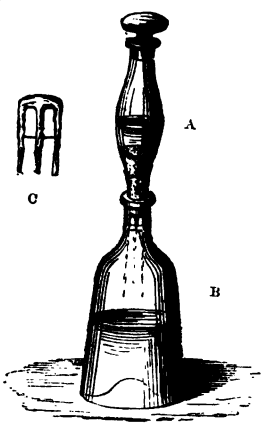


Fig. 156.

759. *Tannic acid*, $C_{18} H_5 O_9$, 3HO, to which the name *tannin* is more particularly applied, is prepared pure by introducing pulverised nutgalls into a pear-shaped glass vessel A, inserted in the mouth of a flask or decanter B, *fig.* 156. To retain the nutgalls in A, its mouth is stopped by a cork C (surrounded by cotton), in the sides of which grooves are cut, through which the liquid slowly passes. Ether of commerce, which contains 10 per cent. of water, is poured upon the nutgalls. The tannin first dissolved by the ether, is then precipitated

in the state of a thick syrup, by the water which the ether contains. The ether and the syrupy solution of tannin collect in two strata in the flask B, the ether being uppermost. The ether is then poured off and passed again through the nutgalls in A, so as to extract more tannin from them. The syrupy solution, after being several times washed with pure ether, is evaporated under an exhausted receiver or at a temperature not exceeding 212°. The residuum is tannin, in the greatest known state of purity.

According to Guibourt, the best solvent for the complete extraction of tannin from nutgalls, is a mixture of 20 parts of anhydrous ether, and 1 part of spirit of wine containing 69 per cent. of absolute alcohol.

Tannic acid is solid, white, and colourless, with a strongly astringent taste. It is soluble in water, and not crystallisable. It is soluble in alcohol and ether, but less so in the latter than in the former. Its aqueous solution reddens litmus and decomposes the alkaline carbonates without effervescence. In solution in water it readily absorbs oxygen from the air, and is transformed into gallic acid, disengaging carbonic acid. This process, which is promoted by the presence of animal matter, constitutes the *tannic fermentation*:—

$$C_{18}H_5O_9,3HO + 8O = 2(\overbrace{C_7HO_3,2HO}^{\text{Gallic acid.}}) + 4CO_2 + 2HO.$$

Tannic acid, when pure and dry, is unalterable in the air, and may be kept in the state of powder, being dissolved when about to be used. It acts sometimes as an acid, and sometimes as a base. With the mineral acids (sulphuric, hydrochloric, phosphoric, arsenic, and boracic) it forms white insoluble compounds. It does not precipitate the organic acids. It forms with bases, compounds which are very sparingly soluble. Solutions of potash, lime, and baryta are precipitated by it. It also precipitates the salts which contain organic alkalies; a property which renders it, in certain cases, useful as an antidote in case of poisoning. When it is desired to isolate an organic base, its solution is treated with tannin, which forms an insoluble tannate. That salt is then treated with lime, the insoluble tannate of lime being produced, and the base being liberated, which is then dissolved in alcohol or ether.

Tannin in solution is completely absorbed by animal membranes, and especially by the skin. An insoluble compound of tannin and animal substance is thus formed. The skin after thus absorbing tannin is said to be *tanned*, and is called *leather*. It is thus rendered nearly impenetrable and impermeable.

Solutions of gelatine are completely precipitated by tannin, giving a white and insoluble precipitate.

In virtue of its property of precipitating most animal substances, it is largely employed in the fabrication of white wine, to coagulate a substance which has received the name of *glaïadine*, which, if not removed, would excite in the wine a viscous fermentation.

Tannin is sometimes used in medicine to arrest hæmorrhage.

760. WRITING-INK is made by the reaction of tannin or nutgalls upon a salt of iron. 2 lb of nutgalls are boiled in 2 gallons of water, the liquor filtered and mixed with 1 lb of sulphate of iron and 1 lb of gum, a little sugar and sulphate of copper being sometimes added. Being exposed for a time in the air the liquor acquires a deep black colour.

The gum is added to prevent the tannate of peroxide of iron from being thrown down as a black precipitate.

Ink thus made is not unalterable. Chlorine and oxalic acid easily efface it, and it is even bleached by exposure to the air. An unalterable ink has long been sought, and the problem has to a certain extent been resolved, by a liquid composed of lampblack held in suspension in gum water, to which small quantities of hydrochloric acid or soda are added. A good ink capable of resisting chlorine, oxalic acid, and washing with a hair pencil or sponge, may be made by mixing ink made according to the usual method, with a little genuine China ink. (Ure.)

761. GALLIC ACID, C_7HO_3, 2HO, is obtained by exposing a solution of tannin to the air, the oxygen of which is changed into an equal volume of carbonic acid :—

$$C_{18}H_8O_{12} + 8O = 2(C_7H_3O_3)4CO_2 + 2HO.$$

This acid is white. It crystallises in confused prisms, with 3 equivalents of water, 1 of which it parts with at 212°, and 2 when crystallised in concentrated sulphuric acid. It is soluble in 100 parts of cold, and three of boiling water. It is highly soluble in alcohol, but only with difficulty in ether. Maintained in fusion at 400°, it acquires the property of precipitating gelatine; a property which it has not when merely in solution. It is not absorbed by the skin. In these negative properties it differs from tannin.

In contact with the salts of iron it comports itself like tannin. In solution it reduces certain metallic salts, such as the perchloride of gold, and nitrate of silver. At 356° it parts with carbonic acid, and leaves a pyrogenous compound, called pyrogallic acid, $C_6H_3O_2$:—

$$C_7HO_3,3HO = C_6H_3O_3 + HO + CO_2.$$

762. THE ART OF TANNING has for its object, to render hides and skins impermeable, elastic, and imputrescible, by causing the animal matter of which they are constituted, to enter into combination with tannin. Thus treated, the hides are converted into leather. Its suppleness and impermeability are augmented by beating and rolling, a process called *currying*.

The skins are first passed through cisterns filled with milk of lime, by which the removal of the hair or fur is facilitated. After being steeped in acid liquor to clear more effectually the pores, they are disposed in alternate layers in pits, with pulverised oak bark, called *tan*, upon which water is poured in sufficient quantity to saturate them. This facilitates the combination of the animal matter with the tannin. The duration of this process, varies from 4 to 8 months, according to the thickness of the hides. The thickest require to be left in the pits from 18 months to 2 years.

763. PECTIN, $C_{44}H_{48}O_{44}$, is the essential principle of vegetable jelly. It may be extracted from various vegetable juices, by precipitation with alcohol. By ebullition with water and with dilute acids it is changed into two isomeric bodies called *parapectin*, and *metapectin*. In contact with bases these three substances are converted into *pectic acid*. By continued boiling with a solution of caustic alkali a further change is produced, and a new acid is obtained, called

metapectic acid, which does not gelatinise. The salts of these acids are incapable of crystallising. Their composition is,—pectic, $C_{32}\ H_{20}\ O_{28}$, 2HO, and metapectic, $C_{24}\ H_{15}\ O_{21}$, 2HO.

CHAPTER XXI.

ORGANIC BASES IN GENERAL.

764. LIKE the mineral, the organic bases combine with acids to form salts, which are generally crystallisable, and in their composition follow the law of definite compounds. The organic alkalies render the syrup of violets green. When they are soluble in water they may be precipitated from their saline solutions by the alkaline or earthy bases, and reciprocally the insoluble metallic oxides may be similarly precipitated by the soluble organic alkalies.

765. When a salt, having an organic base, is submitted to the action of a voltaic current, the acid goes to the positive, and the base to the negative pole.

766. The organic alkalies are usually solid and fixed. Some are capable of forming definite crystals. Several organic bases are liquid and volatile, such as the alkalies of tobacco and hemlock. The solid alkalies are inodorous and fixed, nevertheless cinchonine is volatilised without decomposition, at a moderate temperature. The organic bases generally are sparingly soluble in water, but quite so in alcohol and ether. Some are amorphous, while others, such as codeine, crystallise with remarkable regularity. Their taste is generally acrid and bitter, and they exercise an energetic action on the animal economy. In small doses they are highly valuable medicines, but in larger proportions are active poisons. Bromine and chlorine combine with them to form new bases and hydracids.

767. The bicarbonate of soda precipitates some from their solutions, such as cinchonine, narcotine, strychnine, and veratrine, while it produces no similar effect upon others, such as quinine, morphine, and brucine: it may, therefore, in certain cases be used to separate one base from another.

768. The effects of heat on the organic bases have been but little observed. In general they melt like the resins, producing ammoniacal vapours. Gerhardt has found that, when heated with potash, several were decomposed, producing a peculiar alkaline oil, which he has called *quinoleine*, and which is a mixture of several liquid and volatile bases.

769. The sulphates, nitrates, hydrochlorates, and acetates of the organic bases are generally soluble in water, while the tartrates,

gallates, oxalates, and above all, the tannates are either sparingly so, or totally insoluble. The hydrochlorates generally form double salts with the chlorides of platinum and mercury.

770. Their action on polarised light is often characteristic. According to Bouchardat, these organic alkalies, with the exception of quinoleine, have left-handed polarisation. This power is weakened when they are saturated by an acid, the exception being quinine, which, on the contrary, is strengthened. Narcotine has a singular property in this respect. When pure it has left-handed, but under the influence of acids right-handed polarisation.

771. ORGANIC ALKALIES EXIST NATURALLY in plants, some in a free state, but generally combined with acids forming salts, such as hydrochlorates, malates, lactates, and acetates, and also with peculiar acids, as meconates and quinates. That their presence is not, as was erroneously supposed, due only to the reagents used for their elimination is conclusively proved by the fact, that they have, in certain cases, been obtained by treating the plant with distilled water alone. Dupuy obtained by this means sulphate of morphine perfectly pure from opium.

772. The methods of obtaining the bases from vegetable bodies vary according as they are soluble or insoluble, fixed or volatile.

If the base be insoluble, as is most frequently the case, the vegetable substance is treated with acidulated water, when a salt is formed which is decomposed by ammonia, lime, or magnesia. The organic alkali is separated from the mineral bases employed to precipitate it by ether or alcohol, which dissolves the alkali, and sometimes yields it crystallised in a state of complete purity. It is necessary, however, sometimes to separate the colouring matters from the organic bases, by saturating them with hydrochloric or sulphuric acid, treating the resulting salt with animal charcoal, and then precipitating the base again by an alkali. A second crystallisation generally gives it in a pure state.

If the base be soluble in water, the extraction is much more difficult. Crystallisable salts must then be formed, the acid element of which must then be precipitated.

If the base be volatile, the vegetable substance is distilled with an excess of potash or lime. The base, which passes over, is purified by causing it to pass into saline combinations. The base thus obtained, is generally mixed with ammonia, from which it is separated by saturating the mixture with oxalic or sulphuric acid, and evaporating to dryness. The result is treated with alcohol, which dissolves only the sulphate or oxalate of the organic alkali. This may then be obtained pure by evaporation and crystallisation. The product is then mixed with a solution of potash and an equal volume of ether, when two strata are produced, the uppermost of which is an ethereal solution of the organic alkali. This liquid, distilled in a retort, disengages ether and the last traces of ammonia. The alkali remains in the retort, and can be obtained perfectly pure by a last distillation.

773. ARTIFICIAL BASES constitute one of the most remarkable discoveries of modern chemists. These alkaloids, though possessing singular and important basic properties which place some of them

in close analogy with ammonia, and others with the natural volatile alkaloids, called *nicotine* drawn from tobacco, and *conicine* from hemlock, have never yet been found either in the free or combined state in any natural organic body.

Few of these include oxygen, and nearly all of them volatilise without decomposition.

774. Wöhler first showed that a natural base could be artificially reproduced. That chemist produced *urea*, a nitrogenised compound existing in abundance in healthy urine, by the molecular transformation of cyanate of ammonia :—

$$\overbrace{NH_3,HO,C_2NO}^{\text{Cyanate of ammonia.}} = \overbrace{C_2N_2H_4O_2}^{\text{Urea.}}.$$

775. Liebig obtained three artificial bases, *melamine*, $C_6N_6H_6$, *ammeline* $C_6N_5H_5O_2$, and *ammelide* $C\ N_2H_9O_6$; the first by the distillation of hydrosulphocyanate of ammonia, C_2NHS_2, NH_3, in which process bisulphuret of carbon, ammonia, and sulphuretted hydrogen, are severally expelled. The reaction may be thus stated :—

$$\overbrace{4(C_2NHS_2,NH_3)}^{\text{Hydrosulphocyanate of ammonia.}} = \overbrace{C_6N_6H_6}^{\text{Melamine.}} + \overbrace{2(CS_2)}^{\text{Bisulphuret of carbon.}} + \overbrace{2(HN)_3}^{\text{Ammonia.}} + 4(HS).$$

The last two are obtained by the decomposition of the first by the concentrated acids.

776. *Aniline*, $C_{12}H_7N$, another artificial base, was obtained by Fritzsche, by the distillation of anthranilic acid, $C_{14}H_7NO_4$, an organic compound, resulting from the reaction of potash on indigo :—

$$\overbrace{C_{14}H_7NO_4}^{\text{Anthranilic acid.}} = 2(CO_2) + \overbrace{C_{12}H_7N}^{\text{Aniline.}}.$$

777. *Quinoleine*, $C_{18}H_7N$, an artificial base, was produced by Gerhardt, by distilling certain natural bases, such as *quinine*, *cinchonine*, and *strychnine*, with potash, in which process hydrogen and carbonic acid are disengaged as gases, and quinoleine remains in the receiver :—

$$2(\overbrace{C_{20}H_{12}NO_2}^{\text{Quinine.}}) = 2(\overbrace{C_{18}H_7N}^{\text{Quinoleine.}}) + 4(CO_2) + 10H.$$

But of all the various processes by which chemists have obtained these artificial compounds, the most curious, interesting, and suggestive are those adopted by Zinin and the late Professor Fownes.

778. ZININ'S PROCESS. When fuming nitric acid, NO_5, acts on certain organic substances, a part of their hydrogen combines with an equivalent of the acid, and the nitrous acid, NO_4, which remains, takes the place of the hydrogen thus removed. This reaction is manifested in the case of a great number of

organic substances of every class, acid, neutral, and basic. Zinin showed that if sulphuretted hydrogen act upon nitrogenous products deriyed from neutral bodies, and more especially from certain carburets of hydrogen, sulphur will be deposited and water produced by the combination of the hydrogen of a part of the sulphuretted hydrogen with the oxygen of the organic body, and that the remainder of the hydrogen will be fixed in the new compound, which will have basic properties.

An example of the application of this method is presented in the production of aniline by the action of sulphuretted hydrogen on nitrobenzole or nitrobenzide, $C_{12}H_5NO_4$:—

$$C_{12}H_5NO_4 + 6HS = \underbrace{C_{12}H_7N}_{\text{Aniline.}} + 6S + 4HO.$$

779. FOWNES'S PROCESS consists in the isomeric transformation which compounds, resulting from the action of ammonia on certain volatile oils, undergo in a solution of potash. The oil of bitter almonds and furfurole, a volatile oil obtained by the action of sulphuric acid on bran, present examples of this:—

$$\underbrace{3(C_{14}H_6O)}_{\text{Oil of bit. alm.}} + 2NH_3 = \underbrace{C_{42}H_{18}N_2}_{\text{Benzoline.}} + HO.$$

$$\underbrace{3(C_{10}H_4O_4)}_{\text{Furfurole.*}} + 2NH_3 = \underbrace{C_{30}H_{12}N_2O_4}_{\text{Furfurine.}} + 6HO.$$

780. Benzoline (otherwise hydrobenzamide) and furfurine under the action of alkalies acquire strong basic properties without undergoing any change of composition.

781. To explain the constitution of various organic bases resulting from recent chemical researches, it is necessary to assume the existence of a group of carburets of hydrogen which have received the denominations following:—

Methyle	C_2H_3.	Butyle	C_8H_7.	Amyle	$C_{10}H_{11}$.
Ethyle	C_4H_5.	Valyle	C_8H_9.	Phenyle	$C_{12}H_5$.

These hypothetical compounds are called *alcohol-radicals*; because an ordinary alcohol can always be considered as formed by a combination of the oxide of one of these with a single equivalent of water.

782. If the oxide of the hypothetical metal ammonium be taken as the base of the ammoniacal salts, and if A express generally the acid constituent of the oxy-salts, and B the radical of the haloid salts, the composition of the ammoniacal salts of each class will be expressed thus:—

Ammoniacal oxy-salts	NH_4O, A.
Ammoniacal haloid salts	NH_4, B.

If R, R', R'', R''', ... be taken to express the alcoholic radicals given above, it has been found that one or more of the equivalents of hydrogen in the ammoniacal salts being replaced by an equal number of equivalents of the alcoholic radicals, new salts will be formed. Since the hydrogen may be replaced either by several equivalents of the same, or by single equivalents of different alcoholic radicals, it is evident that a vast variety of artificial organic

* According to some chemists the equivalent of furfurole is one-half more $C_{15}H_6O_6$.

salts may thus be formed, the composition of which may be expressed generally thus:—

	Oxy-Salts.	Haloid Salts.
First group	NH_3RO, A	$NH_2R, B.$
Second group	NH_2R_2O, A	$NH_2R_2, B.$
	$NH_2RR'O, A$	$NH_2RR', B.$
Third group	NHR_3O, A	NHR_3, B
	$NHR_2R'O, A$	$NHR_2R, B.$
	$NHRR'R''O A$	$NHRR'R'', B.$
Fourth group	NR_4O, A	$NR_4, B.$
	$NR_3R'OA$	$NR_3R', B.$
	$NR_2R'R''O, A$	$NR_2R'R'', B.$
	$NRR'R''R'''O, A.$	$NRR'R''R''', B.$

783. The bases of the salts of the first group, having the form NH_2RO, are called *Amidogen bases;* those of the second $NH_2RR'O$, *Imidogen bases;* and those of the third $NHRR'R''O$, *Nitrile* bases.

The fourth group differs from the others in their properties. These salts are not decomposed by potash, but by suitable treatment give a series of compounds of a powerfully alkaline character, the composition of which is $NRR'R''R'''O,HO$, which have an obvious analogy to hydrated ammonia, but which differ from it by their remarkable stability.

How very numerous the salts are which may be obtained by this process, will be apparent from considering the combinations of which the six alcoholic radicals, given above, are susceptible.

784. It has been already explained that all attempts to separate ammonium from its oxide have failed, the decomposition of the oxide being always attended with the decomposition of the hypothetical metal itself.

This property reappears in the artificial compounds, which have received the generic name of *ammonia salts*. In the case of the first three groups the change is perfectly analogous to that produced on the salts of ammonia, properly so called. The oxide separated on the decomposition of the salt is itself decomposed and resolved into water and a volatile base, the properties of which, more or less, resemble those of ammonia itself, according to those of the alcoholic radical which replaces the hydrogen.

785. The following will serve as examples of the nomenclature of this numerous class of compounds:

ETHYLE SERIES. Let ethyle, $C_4H_5=R$. Then *Ethylamine*$=NH_2R$.
Diethylamine$=NHR_2$, and *triethylamine*$=NR_3$.
METHYLE SERIES. Let methyle, $C_2H_3=R$. Then *Methylamine*$=NH_2R$.
Dimethylamine$=NHR_2$ and *trimethylamine*$=NR_3$.
And the same system of nomenclature is applicable to the derivatives of the other hydrocarbons.

Examples of the nomenclature of the mixed bases—Let R=ethyle and R′= methyle, then NHRR′ is ethylomethylamine.

Let R=methyle, R′=ethyle and R″=phenyle. Then NRR′R″=methylethylophenylamine, and so on.

786. A great number of this numerous class of artificial bases has been already produced and their properties demonstrated, and the researches of chemists from year to year are rapidly augmenting the number of them. The purposes and limits of this volume, however, render it impossible here to describe them, and the student who is desirous to pursue the subject, is referred to the ample and lucid statement in Dr. Gregory's Organic Chemistry.

CHAPTER XXII.

THE MOST IMPORTANT ORGANIC BASES.

787. OPIUM is the substance obtained by evaporating the milky juice of the poppy.

The immediate analysis of this compound, one of the most difficult and delicate processes of organic chemistry, gives a considerable number of components, consisting of eight organic bases, *morphine*, *codeine*, *narcotine*, *thebaine*, *pseudo-morphine*, *porphyroxine*, *narceine*, and *papaverine*. It also gives *meconine*, a neutral non-nitrogenous compound, caoutchouc, colouring matters, sulphates, and a peculiar acid called *meconic*.

788. MORPHINE, $C_{34}H_{19}NO_6$, is prepared by very various processes. That of Dr. Gregory is as follows :—

A strong infusion of opium is mixed with a solution of chloride of calcium, free from iron. Meconate of lime, nearly insoluble, separates, while the hydrochloric acid combines with the bases. By filtration and concentration the hydrochlorate of morphine may be obtained crystallised, the narcotine and other constituents remaining behind. The base, morphine, may be precipitated in a pure state by ammonia. Opium contains about 10 per cent. of morphine, which is its chief active principle.

Morphine crystallises in rectangular prisms with bevelled ends, and sometimes in octohedrons. These contain 2 equivalents of water, easily expelled by heat. They are unalterable in air, and fuse at a gentle heat. Heated in air morphine burns like resin, leaving a carbonaceous residuum. Cold water dissolves only 1 part, while boiling water dissolves 10 parts in 1000. Its solution is bitter with an alkaline reaction. It is almost insoluble in ether, and is dissolved by 30 times its weight of boiling alcohol. In virtue of this property, morphine can be separated from the narcotine which accompanies it, the latter being easily dissolved by ether.

The characters of morphine have great importance in forensic medicine. Nitric acid colours it a deep yellow or red, but this property is common to it and brucine. Iodic acid imparts to it, as well in combination as in the free state, a reddish-brown colour, accompanied with the peculiar odour of iodine. By this test, according to Sérullas, the presence of 1 part of morphine in 7000 of a liquor may be ascertained.

The perchloride and sesquioxide of iron impart a deep bluish colour to a solution of morphine, but the colour is not permanent.

789. THE SALTS OF MORPHINE are prepared by the direct action of the acids upon it. They crystallise sometimes with great regularity, are soluble in water and alcohol, and sparingly so in ether. Their taste is bitter and nauseous. In small doses they act upon the animal economy as a narcotic; in large, they

are fatal. The reagents used for the detection of morphine, serve equally for its salts. These salts reduce solutions of gold and silver, and precipitate the bichloride of platinum and iodide of potassium.

790. CODEINE, $C_{35}H_{20}NO_5$, is prepared by dissolving hydrochlorate of morphine, which always contains it, in water with a slight excess of ammonia. The double hydrochlorate of ammonia and codeine remains in the liquor, the morphine being precipitated. This is treated with ether, which dissolves the codeine and allows of its crystallisation.

Codeine restores the colour of litmus-paper reddened by acid, and produces abundant precipitates in the salts of iron, copper, lead, and other metals from which, like the other soluble alkalies, it separates the bases. It crystallises sometimes in octohedrons, and sometimes in large prisms, with the most perfect regularity.

It is very soluble in ether, from which it is often precipitated in fine prisms, containing two equivalents of water of crystallisation easily dismissed by heat. It fuses at 300°, and is distinguishable from morphine, inasmuch, as neither nitric acid nor perchloride of iron colours it. It is moreover completely insoluble in the alkalies, which, therefore, separate it from its solutions. Boiling water dissolves it in considerable quantity, most of it, however, being deposited in cooling, while, on the contrary, morphine is almost insoluble in boiling water.

In its medicinal use, codeine is similar to opium.

791. NARCOTINE, $C_{46}H_{25}NO$, the first base obtained from opium, is prepared by treating the residuum left in the preparation of morphine and codeine, with acetic acid. It may also be obtained by treating opium with ether, which dissolves the narcotine and allows of its crystallisation.

This base crystallises in right rhomboidal prisms, fused at 340°. It is scarcely soluble in boiling-water, and has no action on the colour tests. It does not colour either nitric acid or chloride of iron.

792. CINCHONA, or *Peruvian bark*, owes its medicinal virtues to two alkaline constituents, *quinine* and *cinchonine*. It also contains two other alkaloids in smaller proportions, and of inferior importance, called *quinidine* and *cinchonidine*, which are respectively isomeric with the former.

Three varieties of cinchona are known in commerce, the *gray* or *pale*, the *yellow*, and the *red*. The first yields cinchonine, the second quinine, and the third, both, in nearly equal proportions.

793. QUININE, $C_{20}H_{12}NO_2$,* is prepared from its sulphate which is found quite pure in commerce, by solution in water, and precipitation by ammonia.

* $C_{38}H_{24}N_2O_4$, according to Regnault: $C_{40}H_{24}N_2O_4$, Pownes, and others.

Quinine is sparingly soluble in water, 1 part being dissolved in 400 of cold, and 1 in 250 of boiling water. It is soluble in alcohol and ether, and has the common properties of the organic alkalies. In crystallising, it retains 3 equivalents of water, which it loses at 250°.

794. THE SALTS OF QUININE diluted with water, and treated successively with chlorine and ammonia, take a greenish blue colour. By this quinine is distinguishable from other organic bases.

The oxalate, tartrate, citrate, gallate, and the acid tannate and iodate are very sparingly soluble. The soluble salts are more bitter than those of cinchonine, and are precipitated by the bichlorides of mercury and platinum, and the salts of silver.

795. SULPHATES. If Q be taken to express quinine, the neutral sulphate is, Q, SO_3, HO, and the bibasic or sulphate of commerce is, Q_2, SO_3, 8HO. The latter alone is employed in medicine, and its fabrication constitutes an important branch of industry. It consists of white flexible needles or thin plates, of intensely bitter taste. It is easily fused, and after fusion, when submitted to friction in the dark is phosphorescent. Exposed in the air it effloresces, and loses by degrees three-fourths of its water of crystallisation.

It is sparingly soluble in cold water, 1 part being dissolved by 700, but more so in boiling water, 1 part being dissolved by 30. The neutral sulphate is much more soluble. In preparing the basic sulphate, it is, therefore, necessary to avoid using an excess of sulphuric acid.

The basic sulphate supplied in commerce is sometimes adulterated with sulphate of lime, boracic acid, sugar, the fat acids, starch, salicine, &c. The presence of inorganic impurities may be detected by burning a small portion on a platinum dish. If the article be pure, there will be no residuum.

The presence of stearic acid may be detected by dissolving in water. The salt of quinine alone will be dissolved and the impurity will be deposited.

If salicine be present in the substance it will be reddened when gently heated with sulphuric acid. But if its proportion do not exceed 10 per cent. it will be more effectual to dissolve it in 6 times its weight of concentrated sulphuric acid, and then add 12 parts of water, which will determine the precipitation of the salicine in a state of purity.

If sugar be present, it will be perceived by the odour of caramel, when burnt.

796. CINCHONINE, $C_{20}H_{12}NO$, differs in composition from quinine, merely by one equivalent of oxygen. It crystallises in large quadrilateral prisms, having strong refractive power. It is nearly tasteless, and scarcely soluble in boiling water. When heated it volatilises without decomposition. It is distinguished from quinine by crystallising with much greater facility in alcohol. As a febrifuge it is less efficacious than quinine.

797. STRYCHNOS, *nux vomica*, *St. Ignatius' bean*, and the *false angostura bark*, yield the alkaloids called *strychnine* and *brucine*, which are also found in the poison called the *upas tieuté*.

798. STRYCHNINE, $C_{42}H_{22}N_2O_4$,* crystallises in octohedrons, or quadrilateral prisms, terminated by four-sided pyramids. It has a taste so bitter as to be insupportable, which is strongly felt in a

* $C_{44}H_{24}N_2O_8$, Frémy and Pelouze.

solution which contains no more than 1 part of strychnine in 600,000 of water, and 1 part in a million is still perceptible. It is scarcely soluble in water, 2500 parts of boiling, and 7000 of cold water being necessary for the solution of 1 part of this alkaloid. It is sparingly soluble in alcohol and ether.

Strychnine is one of the most active poisons. It acts strongly on the spinal marrow, producing paroxysms of tetanus. It is used occasionally in doses of a twelfth of a grain in certain cases of paralysis.

Salts of strychnine are more soluble, and still more poisonous, than the uncombined alkaloid.

799. Brucine, $C_{46}H_{26}N_2O_8$, 8HO, crystallises in right rhomboidal prisms, is more soluble than strychnine in water, being dissolved by 500 parts of boiling, and 800 of cold water. It is insoluble in ether, but quite soluble in alcohol. It is a less energetic poison than strychnine, from which it is easily distinguished, nitric acid imparting to it a blood-red colour. This liquor is rendered violet by the chloride of tin. Bromine gives a blue tint to brucine.

800. Caffeine and Theine, $C_8H_5N_2O_2$.* These isomeric alkaloids are the principles which confer their peculiar properties to coffee and tea. Caffeine crystallises in silky needles, containing two equivalents of water, which it loses at 212°. It fuses at 350°, and sublimes about 570°. It is soluble in water, alcohol, and ether. It has feeble basic properties, being soluble in acids, but parting from them on evaporation. Water and alcohol also separate caffeine from the acids.

Theine is white, and crystallises in long silky needles. It combines only with the strong acids, is fusible and volatile. It is soluble in water, alcohol, and ether. Its aqueous solution is precipitated by tannin.

801. Nicotine, $C_{20}H_{14}N_2$,† the essential principle of tobacco, is prepared by digesting with water the leaves of that plant coarsely chopped.

Nicotine preserved in closed tubes is a colourless liquid, which acquires a brown colour when exposed to the air. Its SG = 1·024. It has an acrid odour and burning taste, and is highly poisonous. Its vapour is so extremely irritating, that a single drop evaporated in a room, renders the air scarcely respirable. The density of the vapour is 5·607. (Barral.)

It mixes in all proportions with alcohol, the fat oils, and essences. Its boiling point is 450°. It is a powerful alkali, neutralises all the acids, precipitates from their solutions almost all

* $C_{16}H_{10}N_4O_3$, Payen. † $C_{40}H_{28}N_4$, Barral. $C_{10}H_7N$, Fownes.

the metallic oxides, and is separated from its salts only by ammonia, and the bases of the first two classes §§ 255, 256, alumina excepted.

802. Its salts are very deliquescent. Some, such as the tartrate, oxalate, and phosphate, crystallise slowly in dry air, but better with an excess of acid. Alcohol dissolves them, but they are generally sparingly soluble in ether, with the exception of the acetate.

Nicotine absorbs dry hydrochloric acid, and forms crystalline needles; but the combination is slow, because a crust is formed at the surface which intercepts the action on the remainder of the alkali. When heated it rapidly absorbs the acid and acquires a red colour.

An aqueous solution poured into a solution of corrosive sublimate gives a white precipitate, sparingly soluble, which is a double chloride. When the nicotine has been slightly supersaturated with hydrochloric acid the precipitate is not formed at once, but after some time crystalline needles, formed by the combination of the hydrochlorate of nicotine with the chloride of mercury, appear.

Exposed in dry air nicotine absorbs humidity, but that it has not any strong affinity for water is proved by the fact, that it parts with this water in air kept dry by sulphuric acid, in which it loses at the same time any ether or ammonia it may hold in solution.

It is so poisonous that a small dose suffices to kill quickly a strong animal. Its action on the animal economy resembles that of prussic acid.

803. Coniine, *conicine*, or *conia*, $C_{16}H_{15}N$ * (Regnault), the active principle of hemlock, is prepared from the seeds of that plant by a process similar to that explained for the preparation of nicotine. It is colourless, oleaginous, with SG = 0·89. It has a pungent and disagreeable odour, and boils at 338°. Exposed to the air it resinifies. It is soluble in water, alcohol, and ether. It is highly poisonous, a dose of two grains having an immediate action on the economy. Its salts are acid, uncrystallisable, and poisonous. In pharmacy they are conveniently substituted for the extracts of hemlock, not being alterable.

CHAPTER XXIII.

NEUTRAL BODIES.—WOOD AND ITS CONSTITUENTS.

804. Ligneous Structure. When the woody part of plants and trees is separated from all the matter it contains which is soluble in water, alcohol, ether, dilute acids, and alkalies, there remains a solid structure of cellular form, the walls of whose cavities consist of a fibrous matter, to which the name *cellulose* has been given. The inner surface of these walls are incrusted with a hard amorphous substance, called *lignine*, of varying thickness, according to the age and species of the plant and the part of it in which the cells are placed. In some cases this lining fills nearly the entire cavity of the cell, while in others it forms only a thin

* $C_{16}H_{16}N$, Pelouze and Frémy.

coating, leaving the interior cavity quite open. The open space within this lining is that in which the sap circulates.

805. CELLULOSE, or *cellular tissue*, $C_{12}H_{10}O_{10}$, is common to the cellular structure of all vegetables. Its centesimal composition is—

Carbon	44·44
Hydrogen	6·18
Oxygen	49·38
	100·00

In young plants the cells are formed in the midst of the sap, which circulates in their stalks, and each cell is successively developed in attaching itself to those previously formed. The forms are modified in this process: sometimes they are round, and manifest a certain regularity of arrangement and form, as in the pith of elder, *fig.* 157. In this case they consist of *cellular tissue*,

Fig. 157.

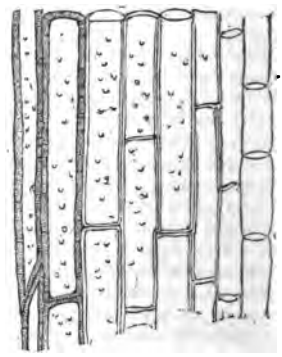


Fig. 158.

properly so called. Sometimes they affect the form of oblong vessels connected at the ends, as is shown in the longitudinal and transverse sections of the stalk of asparagus, *figs.* 158 and 159, and in fibres of hemp or flax, *fig.* 160, or of cotton, *fig.* 161. In such cases they are called *vascular tissue*.

As the plant advances in age the coating of lignine incrusting the inner surfaces of these vessels, becomes thicker and thicker, leaving less and less open space within for the circulation of the sap. This combination constitutes what is familiarly known as *wood*.

Cellulose is almost pure in the hairy matter of the cotton-plant, in hemp, in flax, and in artificial substances derived from these, such as paper, and the rags from which it is made. It is all but absolutely pure in the Swedish filtering papers. To obtain it chemically pure it is only necessary to treat these bodies successively with water, alcohol, ether, the weak acids, and dilute alkalies.

Pure cellulose is white, solid, translucent, insoluble in water, alcohol, ether, and the oils fixed and volatile. Its SG = 1·525.

The dilute acids and alkalies have but little action upon it. Its resistance to these reagents varies with its age, the fresh and recently formed being more easily affected than the old and more cohesive. Concentrated sulphuric and phosphoric acids produce

remarkable effects upon it, converting it first into *dextrine* and then into *glucose*, compounds which will be described hereafter.

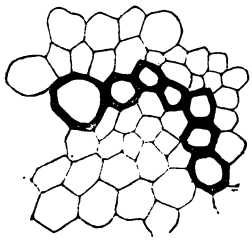


Fig. 159.

Fig. 160.

A mixture of sulphuric and fuming nitric acids converts it into *pyroxyline*, or *gun-cotton*. At a boiling heat nitric acid dissolves it, oxalic acid being formed. Acetic acid is without action on it.

Fig. 161.

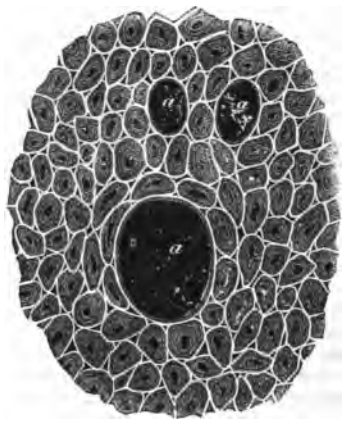


Fig. 162.

When cellulose has been disintegrated by sulphuric acid it is rendered blue by a solution of iodine; a property which indicates its close relation to starch, with which it is isomeric, as will presently appear. This reaction serves to distinguish cellulose from certain nitrogenised membranes, which do not possess this property.

806. LIGNINE, which lines and encrusts the woody cells, is produced from the organic compounds dissolved in the sap. Its structure is illustrated in *fig.* 162, which is a microscopic view of

the transverse section of oak. The black parts show the canals which remain open for the circulation of the sap within the lignine, some of which, such as *a a a*, being much larger than others, are the chief conduits of that liquid.

The structure of the trunk of a tree being produced by the annual formation of matter collecting in a succession of cylindrical shells, one outside another, it follows that the central part is the oldest, and the exterior part immediately within the bark the youngest and most recent. As the incrustation of lignine augments with age, it follows that the central part must always be more dense than the external. The latter, therefore, having more open spaces for the circulation of the sap, is denominated *sap-wood*, the central and more dense part being called the *heart*.

The lignine, being friable, can be separated from the cellulose by bruising and sifting. It contains a greater proportion of hydrogen than the cellulose, and gives more heat in combustion. For the same reason the hard woods, which contain a greater proportion of lignine, have a greater calorific power.

Lignine is blackened by sulphuric acid, and soluble in chlorine. By these properties it is distinguished from cellulose.

807. GENERAL PROPERTIES OF WOOD. Wood is properly more dense than water, and floats only by reason of the air which pervades its pores. Its specific gravity varies: light woods, such as maple or pine, have SG = 1·46, and the more dense, as oak and beech, SG = 1·53. The density, however, varies much, even in the same species, under the influence of age, climate, and soil.

Freshly cut wood contains about 40 per cent. of water. By desiccation at 50° this is reduced to 25 per cent., so that the wood sold as dry wood still contains a fourth of its weight of water. As fuel this greatly impairs its value, since the evaporation of so much water renders latent a great proportion of the heat developed in the combustion of the wood.

The constituents of wood which disappear in combustion are carbon, hydrogen, and oxygen. Certain mineral substances which are incombustible form the ashes. The proportion of these ashes varies, not only in different woods, but in different parts of the same wood. It varies from 4 to a fifth per cent.

The ashes consist of soluble alkaline salts, formed by the combination of potash and soda with carbonic, sulphuric, and hydrochloric acids; and of insoluble compounds, which contain carbonic and phosphoric acids, lime, magnesia, the oxides of iron, manganese, and silica.

Submitted to heat in close vessels wood begins to be decomposed at 284°. The products of its distillation vary with the species of wood and the temperature. Inflammable gases, water holding acetic acid and wood spirit in solution, acetate of methyle, and various tarry substances are constantly produced. The gases disengaged are carbonic acid and oxide, hydrogen and nitrogen. The residuum is charcoal, which retains the form and structure of the wood, the quantity varying from 13 to 28 per cent. of the total weight of the wood.

Woods of close and compact texture, such as oak, beech, and elm, are consumed more slowly than the white woods, and yield a greater proportion of charcoal. The charcoal of the lighter woods burns more rapidly and in flames.

Wood is rotted by exposure to air and moisture. In this process it changes colour, is disintegrated, and combines partially with the oxygen of the air to form carbonic acid, the residuum being vegetable mould and peat.

808. PEAT is, in fact, the result of the change which aquatic herbaceous plants undergo in marshy places. It is found in thick horizontal beds, in which

articles of pottery and other utensils are sometimes found, which attest its modern origin.

809. FOSSIL COMBUSTIBLES. These may be classed as *lignite*, *coal*, and *anthracite*. Lignite is found in the most recent geological deposits composing the tertiary rocks, and coal and anthracite in the secondary and transition series. All are evidently fossilised vegetables, the traces of their original structure being everywhere apparent.

The constituents of all fossil combustibles are carbon, hydrogen, oxygen, azote and incombustible ashes, in variable proportions, the mean of which is nearly as follows :—

	Carbon.	Hydrogen.	Oxygen and Nitrogen.	Ashes incombustible.
Welsh anthracite	91·29	3·33	4·80	1·58
Newcastle coal	86·75	5·24	6·61	1·40
Cannel coal (Lancashire) . . .	82·60	5·66	9·19	2·55
Lignite (Dax)	69·52	5·59	19·90	4·99

The heating power of coal increases with the proportion of carbon it contains. That of anthracite is nearly equal to charcoal.

Coal gives by distillation water, combustible gases, ammonia, empyreumatic oils, and tar, containing a solid carburet of hydrogen, called *naphthaline*.

810. PRESERVATION OF WOOD. Considering the extensive use of timber the art of preserving it from destruction by dry rot and other agencies, acquires the highest importance. Several causes produce its decay and destruction, such as the action of air and moisture, the attacks of insects, and the effects of certain cryptogamous and fungous plants, which grow upon its surface and often strike their fibres into its innermost parts. One of the immediate constituents of wood is a nitrogenous compound, which acts as a ferment, supplies food for the destructive insects, and a sort of manure for the fungous plants which grow upon and tend to destroy it.

The means of preservation therefore, however they may differ from each other, agree in having for their object to displace this nitrogenous compound which lies in the sap-vessels, and to substitute for it some substance which has opposite properties. Various substances are found to serve this purpose, such as the essences, creosote, pyroligneous acid, sulphate or acetate of iron, bichloride of mercury, sulphate of copper, and arsenic.

Various expedients have been adopted to make the solutions of these compounds penetrate the timber and fill its capillary vessels. Intense hydraulic pressure was first applied, but the process was too expensive. Soakage in cisterns required a long period of time and was neither sufficiently effectual nor sufficiently economical.

The natural agency of the sap-vessels themselves has been applied with great ingenuity, and it would seem with much success, by MM. Bréant and Mohl, and more especially by M. Boucherie. An incision around the trunk near the root is made with a saw, and surrounded with the solution to be imbibed, the surface of the liquid being above the incision. The lateral branches are lopped off, those at the top of the tree with their foliage remaining in order to draw up the liquid through the sap-vessels. By this expedient the capillary vessels of the tree are soon filled with the solution, the sap being expelled from them.

Thus a poplar, the trunk of which was about 50 inches circumference, absorbed in 6 days 66 gallons of pyroligneous acid; a plantain 40 inches absorbed 44 gallons of the solution of the chloride of calcium in 7 days.

It was found by the directors of the works in the forest of Compiègne, that a beech-tree, measuring 294 cubic mètres or about 10,400 cubic feet, discharged 673 gallons of sap, which were replaced by 706 gallons of pyroligneous acid. This interesting experiment supplied incidentally the means of estimating the ratio of the volume of the saturated wood to the liquid sap which it includes.

By introducing into the vessels of wood in this manner, solutions, which by mutual decomposition produce colouring principles, materials for ornamental cabinet work have been obtained. Thus with salt of iron and tanning matter, prussiate of potash, acetate of lead, chromate of potash, various coloured veins and streaks, black, gray, blue, yellow, brown, green, and other tints, capable of endless variety may be obtained.

Railway sleepers, prepared by this method, have been laid down alternately with those of the unprepared timber; and on examining both after a lapse of several years, the latter were found to be completely decomposed, the former remaining perfect.

811. PAPER MANUFACTURE. Cellulose is the material of paper. To obtain it old rags are ripped, unravelled, subdivided, soaked in a lye, and thus reduced to the state of pulp. This pulp is then bleached by chlorine, either free or combined with lime, care being taken not to apply that agent in such excess as to injure the texture of the cellulose. The pulp thus prepared is then reduced to a thin sheet of indefinite length, which is subsequently cut into smaller sheets by suitable mechanism. This latter process, involving mechanical and physical principles only, need not be detailed here.

To destroy the porosity of the paper, so as to prevent the ink from soaking into it and thus spreading into blots, it is submitted to the process of *sizing*, which consists in soaking it in a solution of gelatine and alum, the use of the alum being to precipitate the nitrogenised substance which fills the pores of the paper. The sizing substance generally applied consists of a mixture of starch with a compound of resin and alumina, which in the improved processes of the manufacture is applied to the pulp before the latter is reduced to sheets.

812. PYROXYLINE, or GUN-COTTON. If cellulose in any state, as cotton, hemp, flax, thread, paper, &c., &c., be immersed for some minutes in concentrated nitric acid and then withdrawn and washed in abundance of water, it will retain its form and state without observable change, but will acquire the property of excessive combustibility. This substance has been called *pyroxyline*.

Raw cotton or cotton wool, as it is sometimes improperly called, prepared in a like manner, constitutes the substance known as *gun-cotton*, being applicable to firearms and blasting as a substitute for gunpowder.

The best method of preparing gun-cotton is to immerse carded cotton stove-dried in a mixture of 3 volumes of concentrated nitric acid, SG=1·500, with 5 of sulphuric acid of commerce. After remaining 15 to 20 minutes in the acid, the cotton is withdrawn, compressed, washed with abundance of water until it no longer retains either taste or odour, and exercises no action on litmus paper. When compressed with a linen cloth and divided by the fingers or carded, it is easily dried at common temperatures. The process may, however, be expedited by exposing it to a current of dry air at 80° to 100°, or placing it near some hygrometric substance, such as quicklime.

100 parts of pure cellulose thus treated produce 175 of pyroxyline.

CHAPTER XXIV.

STARCH.—SUGAR.—GUM.

813. STARCH is a substance universally diffused in the vegetable world and found also in the animal organism. It is found in the seeds, roots, tubers, pitch and bark, in pulpy fruits, in the expressed juice of most vegetables, and also in the blood, brain and other parts of the animal organism. The common starch is derived from wheaten flour, fecula or potato starch from that root. *Tapioca*, derived from the root of *Jatropha manihot*, *arrow-root* from that of *Maranta arundinacea*, *sago* from the stem and pitch of *Sagus farinifera Rumphii*, are severally mere varieties identical with starch in their chemical composition.

814. If flour be mixed up and kneaded in a cloth with water, a whitish liquid will be strained off which, being left to settle, will deposit starch. The substance retained by the cloth, called *gluten*, which is white and insoluble in water, is nitrogenous, and is the constituent on which the value of meal as an article of food chiefly depends.

Fig. 163.

815. Starch is a snow-white glistening powder, which crackles between the fingers. When submitted to the microscope it appears to consist of transparent ovoidal grains, the magnitude of which varies in different plants, those of the potato being greatest, those of leguminous seeds, such as peas less, and those of wheat and rice smaller still.

When the fecula of the potato is submitted to the microscope it presents the appearance shown in *fig.* 163. Each grain presents at its surface a peculiar point *a* called the *hile*, round which the matter is disposed concentrically in layers or strata with a certain regularity. If a grain be compressed between two slips of glass it will be broken into several fragments, *fig.* 164, the planes of fracture having their common intersection in the hile. Each grain consists

Fig. 164.

Fig. 165.

of a succession of thin pellicles, which may be exfoliated by heating the fecula to about 400°, *fig.* 165.

The symmetrical arrangement of the amylaceous molecules around the hile is

Fig. 166.

rendered very apparent when the grains of fecula are submitted to polarised light, and a prepared rhomb of Iceland spar is interposed between the object and the eye. A black cross is then observed, the centre of which coincides with the

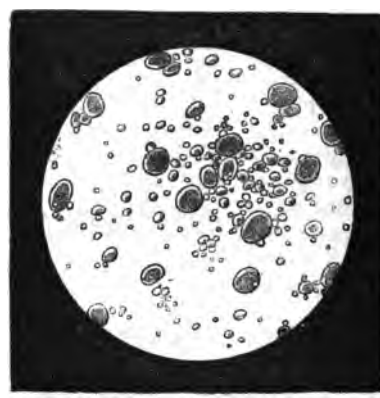


Fig. 167.

hile, and which is analogous to those which are seen through thin crystals, having a single axis at right angles to which they have been cut.* The grains already shown in *fig.* 163 by common light, assume in polarised light, when viewed in the manner here explained, the appearance shown in *fig.* 166.

The amylaceous granules of different vegetables present different appearances,

* H. B. Nat. Phil., "Optics" (286).

by which they may be easily identified by a practised eye. This is rendered apparent by inspecting *figs.* 163, 167, 168, and 169, the first showing the granules of the potato, the second those of wheat, the third of peas (*a* dry and

Fig. 168.

b green), and the fourth those of maize. The fecula of the potato is more certainly and easily distinguished, being the only amylaceous granule which gives the black cross with polarised light.

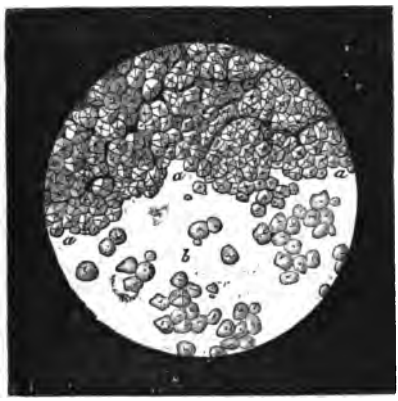


Fig. 169.

The following are the relative magnitudes of the granules of different vegetables expressed, in their lengths, in hundred thousandths of an inch :—

Potato . .	740	Wheat . .	180	Millet .	40
Bean . . .	300	Spanish potato	160	Parsnip . .	28
Sago . .	200	Maize . . .	100	Grain of Beet .	16

If starch be put in 15 times its volume of water, of which the temperature is then gradually raised, a part of the granules will begin to dilate, and will burst when the temperature rises to 140°. This disintegration is accelerated as the temperature is further elevated, and when it approaches 212° all the granules are exfoliated and so enlarged that they fill the entire volume of the liquid, which is thus transformed into the gelatinous paste* used for starching linen and pasting and sizing paper.

The conversion of the fecula into gelatinous paste is accelerated by adding 1 or 2 per cent. of caustic potash or soda to the water.

816. When the dilute acids act on starch at 212° the amylaceous matter is immediately disintegrated, and an isomeric change ensues, the result of which is, first, the production of a soluble substance, called *dextrine*, because it possesses right-handed polarisation,† and then into *glucose*, or grape sugar, which has the same optical property.

Starch is quite insoluble in alcohol at any temperature. Though generally regarded as neutral, it is capable of combining with certain bases, such as lime, baryta, and oxide of lead.

817. Iodine exercises a characteristic action on starch, producing a dark blue colour, which varies in tint with the state of aggregation of the starch. It is generally blue, but sometimes violet, and when the starch has undergone partial disintegration it becomes red. Exposed to light the iodide of starch is discoloured, the iodine being converted into hydriodic and iodic acids (Guibourt). When iodide of starch in suspension in water is raised to a temperature of 150° it becomes colourless, but recovers its colour when cooled (Lassaigne).

818. When iodide of starch is discoloured by exposure to solar light, the colour may be restored by some drops of chlorine, which, decomposing the hydriodic acid, liberate the iodine, which again combines with the starch and colours it. Alkaline solutions seizing on the iodine also discolour the iodide, the colour being restored by an acid, which, seizing on the alkali, liberates the iodine.

Neither acetic acid nor ammonia has any action on starch.

Fuming nitric acid forms with starch a compound called *xyloidine*, insoluble in water.

819. Cellulose, which is isomeric with starch, is not rendered blue by iodine; but if it be put for some moments in contact with sulphuric acid it will be

* A term is wanted in English to express starch in this state. In French the word *amidon* expresses dry or solid starch, and *empois* starch in the state of gelatinous paste, in which it is used in the laundry. Both these terms, so very different in their signification, are rendered in the dictionaries by the same word *starch*.

† H. B. Nat. Phil., "Optics," Chap. xii.

coloured like starch. Thus it appears that under the influence of this acid cellulose passes into a state in which it acquires the properties of starch.

820. Sulphuric acid, in virtue of the property already noticed, is used to modify starch. If 500 parts of starch be treated with 1000 of water, and 10 of sulphuric acid, and the liquor be heated by transmitting through it a current of steam, the starch will be rapidly dissolved. If the acid be then saturated by carbonate of lime, either dextrine or sugar will be found in the liquor. The composition of these substances is—

Starch $C_{12}H_9O_9$, HO | Dextrine $C_{12}H_9O_9$, HO. | Glucose or sugar $C_{12}H_9O_9$, 3HO.

From this it is evident that the conversion of starch into sugar consists in mere hydration.

821. DIASTASE. In the germination of certain grain, as barley, oats, and wheat, a substance is developed near the shoots and roots, which has the peculiar property of disintegrating starch and transforming it first into *dextrine*, and next into glucose. This substance (discovered by MM. Payen and Persoz) has been called *diastase*.

To prepare diastase, barley in a state of germination is treated with water at 75° to 85°, which dissolves the diastase, and also a nitrogenised constituent, to coagulate which the liquor is then raised to 170°, after which the diastase is precipitated by absolute alcohol.

Diastase is uncrystallisable, soluble in water, and insoluble in alcohol. It is not precipitated by acetate of lead. At 160° it rapidly disorganises starch, transforming it first into dextrine and then into sugar. Payen and Persoz ascertained that 1 part of diastase suffices to change 2000 of starch.

In beer-brewing, when germinating barley is put into water at 160°, its diastase transforms its starch into glucose, which being then fermented, imparts its alcohol to the beer.

822. DEXTRINE, $C_{12}H_9O_9$, HO, isomeric with starch, is solid, soluble in water, and uncrystallisable. It is insoluble in alcohol, and is precipitated from its solution by acetate of lead. It is prepared by the conversion of starch under the influence of acids or diastase.

It is used as a substitute for gum in almost all the applications of that substance, in calico-printing, sizing of paper, &c. It is also used in surgery for bandages which in drying become hard, and can be removed by warm water.

823. GLUTEN is a nitrogenous substance which remains after the starch has been separated from the flour or meal of various sorts of grain. The hardest grains are those which are richest in gluten, as well as in fatty matters, inorganic salts, and cellulose, and are the poorest in starch.

When gluten is boiled, first with pure and then with diluted alcohol, a great proportion of it is dissolved, and a fat filamentous substance remains, which, having a close analogy to animal fibrine, has been called *vegetable fibrine*. The alcoholic liquor deposits in cooling a substance which seems identical with

caseine; reduced by concentration to a syrupy consistency and precipitated by water a white albuminous substance is obtained, which has been called *glutine*.

Gluten is therefore a substance of complex composition, and one to which flour owes its elasticity and consistency, and which renders paste porous when gaseous bodies, generally carbonic acid, are developed in it.

824. SUGAR is the general name of a class of bodies which are soluble in water, have a characteristic sweetness, and are capable of yielding alcohol by fermentation. They are extensively diffused throughout the vegetable kingdom, and are found also in certain animal fluids.

Sugars may be grouped in four classes: 1°, *cane sugar*; 2°, *grape sugar*; 3°, the *sugar of acid fruits*, called also uncrystallisable sugar; and, 4°, the *sugar of milk*.

All these consist of carbon, combined with water in different proportions as follows:—

Cane sugar	$C_{12}H_{11}O_{11} = C_{12}W_{11}$.
Grape sugar	$C_{12}H_{14}O_{14} = C_{12}W_{14}$.
Uncrystallisable sugar Sugar of milk	$C_{12}H_{12}O_{12} = C_{12}W_{12}$.

It appears, therefore, that uncrystallisable sugar would be converted into cane sugar by dismissing 1, and into grape sugar by receiving 2 equivalents of water.

825. Sugar of milk is isomeric with the sugar of acid fruit, but differs from the latter in being crystallisable. According to some authorities the equivalent of sugar of milk is $C_{24}W_{24}$, being double that of uncrystallisable sugar.

826. CANE SUGAR, $C_{12}H_{11}O_{11}$, known from all antiquity, exists naturally in the sugar-cane, the root of beet, the ascending sap of the maple, and the descending sap of the birch, the pumpkin, the turnip, the carrot, the stalk of maize, and in a great number of the sweet tropical fruits, such as the cocoa and the pine-apple.

Cane sugar crystallises in rhomboidal prisms, with dihedral summits. Its SG = 1·6. It is soluble in a third of its weight of cold, and in any proportion of boiling water. Weak alcohol easily dissolves it, but it is almost insoluble in anhydrous alcohol. It fuses at 356°. It is not precipitated from its solution, either by the neutral or subacetate of lead; a circumstance which supplies the analyst with the means of separating it from different organic bodies, which are precipitated by these reagents. Fused or dissolved in water it has right-handed polarisation.

827. If a concentrated solution be rapidly evaporated, a thick liquid is obtained, which can be cast into solid cakes upon a cold surface, forming *barley-sugar*. This is translucent and amorphous, but when kept for some time in close flasks it becomes opaque and crystalline, and returns to the state of common sugar. This change may be retarded by the addition of a small quantity

of vinegar. Sugar is therefore a dimorphous body, and may in this respect be compared with sulphur, which, when suddenly cooled after being raised to 302°, remains soft for some time, and then returns to its original state.

Sugar becomes phosphorescent by percussion. When submitted to friction with a hard surface, it acquires a disagreeable taste.

828. According to Venzke, sugar kept for a long time at its point of fusion assumes new properties, being rendered uncrystallisable and having no action on polarised light. In this state it is called *syrup-sugar*.

829. Water exercises a chemical action on sugar. Under the influence of heat it hydrates it, and converts it into glucose.

$$C_{12}H_{11}O_{11} + 3HO = C_{12}H_{14}O_{14}.$$

This is a fact of considerable importance in the sugar manufacture, for if the syrups be left too long in ebullition, a part of them absorbs water and is converted into glucose, thus deteriorating the saccharine strength of the article.

830. The mineral acids, even when largely diluted, and most of the organic acids transform cane sugar into uncrystallisable sugar, the former having right, and the latter left-handed polarisation.

Cane sugar forms crystallisable compounds called *saccharates*, and it appears from the properties manifested by these, that when anhydrous they contain $C_{12}H_9O_9$, and that in their crystallised state they include 2 equivalents of water of crystallisation, so that the composition of sugar should be expressed thus :—

Anhydrous cane sugar $C_{12}H_9O_9$. | Crystallised $C_{12}H_9O_9$, 2HO.

831. The chief part of the sugar consumed for domestic purposes and in the arts is produced from the sugar-cane. The canes are crushed between rollers, the juice being discharged into pans, in which it is slowly heated nearly to its boiling point. Some water is then added, by which a coagulum is separated, consisting chiefly of earthy phosphates, a peculiar albuminous principle, and mechanical impurities. The remaining clear liquid is next evaporated in open pans, and the syrup, sufficiently concentrated, is transferred to a shallow vessel and left to crystallise, being stirred from time to time to accelerate the process and prevent the formation of large crystals. The dark-coloured uncrystallisable syrup, known as *molasses*, is then drained off, and the residue sent into the market as *raw*, or *muscovado* sugar.

This coarse sugar is refined by dissolving it in water, and adding to it either the serum of blood, or white of egg (albumen), and sometimes a little lime-water, and raising the mixture to the boiling point. The albumen coagulating forms a sort of fibrous mass, by which all the impurities mechanically suspended are brought down. The solution is then rendered clear and colourless by filtration through animal charcoal, evaporated to the crystallising point, and poured into conical-shaped earthen moulds, when it soon solidifies into a confusedly crystalline mass, which after being drained, washed with a little clean syrup, and stove-dried, forms the *loaf-sugar* with which every one is familiar.

When the crystallisation is allowed to take place without stirring the syrup, the crystals acquire a much larger size, and more regular structure, forming the article known as *sugar-candy*.

Sugar produced from the sugar cane is manufactured chiefly in the West Indies, the southern parts of the United States, South America, the East Indies, and China.

Sugar is produced from beet-root in France and some of the German states, and from maple, but only for local consumption, in North America.

832. GRAPE SUGAR, *glucose*, or *starch sugar*, $C_{12}H_{14}O_{14}$, exists ready formed in abundance in the vegetable kingdom. It is found in honey, in the juices of acid fruits, and chiefly of the grape, and forms the white crystalline powder which covers plums and figs. It is obtained artificially by the action of weak acids on various neutral compounds, such as lignine, starch, gum, and sugar of milk. It is this which imparts its peculiar character to the urine of patients suffering from diabetes.

It is apparent that in composition it differs from cellulose and starch, only by the water it includes.

$$\underbrace{C_{12}H_{14}O_{14}}_{\text{Glucose.}} = \underbrace{C_{12}H_{10}O_{10}}_{\text{Cellulose.}} + 4HO = \underbrace{C_{12}H_{9}O_{9}}_{\text{Starch.}} + 5HO.$$

833. UNCRYSTALLISABLE, or FRUIT SUGAR exists exclusively in the acid juices of vegetables, and chiefly in fruits, such as grapes, currants, cherries, plums, &c. To extract it, the expressed juice is saturated with chalk, boiled with white of egg, which clears it of mucilaginous matter, and after filtration evaporated at a gentle heat. The matter resulting has the appearance of gum, is very deliquescent, is soluble in water, and even in alcohol at 33° of Gay Lussac's alcoholometer, but is insoluble in absolute alcohol. It is found ready formed in the descending sap of the maple, and the ascending sap of the birch. Contrary to cane sugar, it has left-handed polarisation.

According to Mitscherlich, cane and grape sugars can be converted into uncrystallisable sugar, when submmitted to the influence of acids.

834. SUGAR OF MILK, or *lactine*, or *lactose*, as it is sometimes called, is obtained by "turning" milk with an acid, so as to coagulate its caseine, then filtering and evaporating the whey, which will deposit the sugar of milk in a very hard, semitransparent, crystalline crust on the sides of the vessel. In Switzerland this is prepared on a large scale from the whey left after the extraction of the Gruyère cheese from the milk.

It is owing to the presence of this that milk has its peculiar sweetness. Its SG = 1·543. It is dissolved by 6 parts of cold, and 2 of boiling water. It is insoluble in alcohol and ether, and unalterable in air. The dilute acids convert it into glucose, and the concentrated, colour it, producing ulmic acid. Nitric acid converts it into mucic acid, $C_{12}H_8O_{14}$, 2HO, and oxalic acid, C_2O_3, HO.

835. GUMS are a class of neutral substances, analogous in their composition to starch and sugar, being soluble in water, by which they are considerably swollen, insoluble in alcohol and ether, and uncrystallisable. They differ from amylaceous compounds generally, inasmuch as they are converted by the action of nitric acid into oxalic acid, and a peculiar acid called *mucic acid*, while the same reagent converts amylaceous compounds into oxalic acid only.

836. Gums are of three sorts : 1°, *arabine* ; 2°, *cerasine* ; and 3°, *bassorine*. ARABINE is the essential principle of gum Arabic,

and is by far the most important compound of this class. Cerasine is the principle of the gums which exude from the common fruit-trees, and bassorine is the essential principle of gum tragacanth, which exudes from certain plants called *astragals*, cultivated in the East.

Gum Arabic exudes in a state of viscous solution from certain species of acacias. It coagulates and hardens on the tree. It is supplied chiefly from Senegal. It is formed in small round lumps of conchoidal and vitreous fracture, of a dull sweetish taste, soluble in all proportions in water, the solution being characterised by a peculiar consistency, termed *gummy*. Evaporation renders the solution first viscous, and finally leaves a solid transparent mass, without the least trace of crystallisation.

When dried at 212° the composition of gum is $C_{12}H_{11}O_{11}$, isomeric with cane sugar. Heated to 264° it loses 1 equivalent of water, and becomes isomeric with starch, $C_{12}H_{10}O_{10}$. Its SG = 1·4. It generally contains 2 to 3 per cent of inorganic matter.

Acids transform it first into dextrine, $C_{12}H_{10}O_{10}$, by depriving it of an equivalent of water, and next into glucose, $C_{12}H_{14}O_{14}$, by imparting to it 3 equivalents.

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837. The group of neutral organic compounds which have been briefly noticed above, are remarkable for the numerous and curious cases of isomerism which they present, for their feeble tendency to form combinations, and as consisting of carbon and water combined in various proportions. If W be taken to express a single equivalent of water, so that W = HO, the general composition of this class may be expressed by the formula, C_nW_m, and since C = 6, and W = 9, it follows that the actual analysis will be—

Carbon . . . . 6n. | Water . . . 9m.

It is easy from this to find the number of parts by weight of carbon and water, which go to the composition of an hundred parts of each compound.

	100 PARTS CONTAIN	
	Carbon.	Water.
Cane sugar—Gum Arabic	42·07	57·93
Grape sugar—Starch	36·38	63·62
Uncrystallisable sugar—Sugar of milk—Starch, dried at 68°	40·00	60·00
Cellulose—Dextrine—Gum, dried at 264°	44·44	55·56

Independently of the curious cases of isomerism here presented, what can be more remarkable than the fact, that cotton-wool, rags, wood fibre, and starch, differ from each other, and from sugar in nothing except the proportion of water they contain, and that all of them may be viewed as combinations of pure charcoal and water in different proportions.

CHAPTER XXV.

ALCOHOLS.—ETHERS.

838. ALCOHOLIC FERMENTATION. The composition of alcohol being $C_4H_6O_2$, it follows that uncrystallisable or fruit sugar, $C_{12}H_{12}O_{12}$, may be regarded as a compound made up by the combination of 2 equivalents of alcohol and 4 of carbonic acid—

$$C_{12}H_{12}O_{12} = 2(C_4H_6O_2) + 4CO_2;$$

and consequently, if any means can be found to separate four equivalents of carbonic acid from their sugar, without decomposing the residuum, that residuum will be alcohol.

This object is attained by the influence exerted by the presence of a body called a *ferment*. Such a body acts merely by its presence in exciting the decomposition, without taking any direct share in the change produced. The compounds into which the sugar is resolved neither give anything to the ferment nor take anything from it.

Besides the presence of a ferment, three other conditions are indispensable to the production of fermentation: 1°, a temperature of 50° to 90°; 2°, the presence of water; 3°, the contact of air, or at least of oxygen.

All sugars are not fermented with equal facility. The uncrystallisable fruit sugar, characterised by left-handed polarisation, is susceptible of immediate conversion into alcohol and carbonic acid. Before the other sugars can be fermented they must be converted into this uncrystallisable sugar, glucose, by dismissing 2 equivalents of water, and cane sugar by absorbing 1 equivalent.

$$C_{12}H_{14}O_{14} = C_{12}H_{12}O_{12} + 2HO = 2(C_4H_6O_2) + 4CO_2 + 2HO.$$
$$C_{12}H_{11}O_{11} + HO = C_{12}H_{12}O_{12} = 2(C_4H_6O_2) + 4CO_2.$$

This previous change has been ascertained by inversion of the power of polarisation. Dubrunfaut and Soubeiran showed that in a fermentation which had recently commenced, a quantity of alcohol being added sufficient to coagulate the ferment and paralyse its action, the sugar still unfermented which remained in the liquor was not cane sugar, but the fruit sugar, whose composition is $C_{12}H_{12}O_{12}$.*

To demonstrate experimentally the process of fermentation it is only necessary to introduce into a flask a mixture of 5 to 6 parts of sugar, 20 to 25 of water, and a small quantity of barm as a ferment, and to keep the mixture for some time at a temperature of 75° to 85°. An abundant disengagement of carbonic acid will then take place. The gas thus evolved may be collected in

* A different view of the phenomenon is adopted by Fownes. Manual, p. 417. Ed. 1856.

the usual manner in receivers, and by submitting the remaining liquid to distillation the product will be found to be alcohol.

That the influence of the ferment acts by immediate contact with the fermenting body may be demonstrated by the following experiment: Let a large glass tube, *a*, *b*, *fig.* 170, covered at one end *b* with permeable paper, be inserted through a cork into a flask A, containing a solution of sugar. Let a small quantity of beer barm, diluted with water, be poured into the tube *a b*. An active fermentation will immediately commence in the tube, attended with an abundant evolution of carbonic acid, while nothing of the same kind will be manifested in the liquid in the flask, which will remain indefinitely unaltered. In this case the saccharine solution penetrating the paper by the principle of endosmose, comes into direct contact with the ferment, and fermentation ensues; but although the ferment is separated from the solution in the flask only by the permeable paper, no fermentation will take place there.

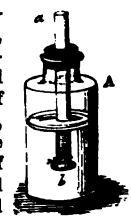

Fig. 170.

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839. ALCOHOLS IN GENERAL. The term alcohol, first limited to the volatile inflammable liquid resulting from the fermentation of sugar, has, in the progress of science, received a much more extended application, being now applied to a certain number of compounds, which in their composition and general properties present a close analogy with alcohol, properly so called. The four following are compounds of this class—

1. Common, or vinic, alcohol . . . . . $C_4H_6O_2$.
2. Wood spirit or methylic alcohol . . . . . $C_2H_4O_2$.
3. Essential oil of potatoes, or amylic alcohol . . . . $C_{10}H_{12}O_2$.
4. Ethal or ethalic alcohol . . . . . $C_{32}H_{34}O_2$.

All alcohols submitted to an oxidising body lose 2 equivalents of hydrogen, which are replaced by 2 of oxygen, a monobasic acid being formed.

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}} + 4O = \overbrace{C_4H_3O_3, HO}^{\text{Acetic acid.}} + 2HO.$$

$$\overbrace{C_2H_4O_2}^{\text{Wood spirit.}} + 4O = \overbrace{C_2HO_3, HO}^{\text{Formic acid.}} + 2HO.$$

$$\overbrace{C_{10}H_{12}O_2}^{\text{Oil of potato.}} + 4O = \overbrace{C_{10}H_9O_3, HO}^{\text{Valerianic acid.}} + 2HO.$$

$$\overbrace{C_{32}H_{34}O_2}^{\text{Ethal}} + 4O = \overbrace{C_{32}H_{31}O_3, HO}^{\text{Ethalic acid.}} + 2HO.$$

840. Alcohol may also, by the action of oxidating bodies, lose 2 equivalents of hydrogen, which combine with 2 of oxygen to form water. The dehydrated alcohol thus obtained is called *aldehyde*.

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}} + 2O = \overbrace{C_4H_4O_2,}^{\text{Aldehyde.}} + 2HO.$$

841. **Aldehyde** is a compound intermediate, by its composition and properties, between the alcohols and the monobasic acids indicated above.

Submitted to the influence of bodies which have a strong affinity for water, such as sulphuric acid, chloride of zinc, or anhydrous phosphoric acid, alcohols have a tendency to lose 2 equivalents of water, and thus to be converted into carburets of hydrogen.

$$C_4H_6O_2 = \underbrace{C_4H_4}_{\text{Ethylene.}} + 2HO.$$

$$C_2H_4O_2 = \underbrace{C_2H_2}_{\text{Methylene.}} + 2HO.$$

$$C_{10}H_{12}O_2 = \underbrace{C_{10}H_{10}}_{\text{Amylene.}} + 2HO.$$

$$C_{32}H_{34}O_4 = \underbrace{C_{32}H_{32}}_{\text{Cetene.}} + 2HO.$$

842. Under the influence of dehydrating bodies, the alcohols may also be reduced to ethers by losing 1 equivalent of water. In this way :—

$$C_4H_6O_2 = \underbrace{C_4H_5O}_{\text{Ether.}} + HO.$$

$$C_2H_4O_2 = \underbrace{C_2H_3O}_{\substack{\text{Methylic ether,}\\ \text{\&c. \&c.}}} + HO.$$

843. Alcohol may be dehydrogenated and reduced to aldehyde by chlorine :—

$$C_4H_6O_2 + 2Cl = \underbrace{2C_4H_4O_2}_{\text{Aldehyde.}} + 2HCl.$$

844. Of all the reagents none give more distinct and important results in their action on the alcohols than the acids. It will suffice here to show the effects of their reaction on the common alcohols.

1°. When alcohol, $C_4H_6O_2$, is submitted to the action of an acid having a strong affinity for water, such as sulphuric acid, either olefiant gas, C_4H_4, or ether, C_4H_5O, will be formed, according to the proportion of the acid employed, either 2 or 1 equivalent of water being absorbed by the acid.

2°. By the action of the hydracids an equivalent of water is absorbed, and the remaining equivalent of oxygen is replaced by an equivalent of the metalloid of the hydracid. A series of ethers, corresponding to vinic ether, are thus produced :—

Chloride of ethyle . .	$C_4H_5, Cl.$	Iodide of ethyle . .	$C_4H_5, I.$
Bromide of ethyle . .	$C_4H_5, Br.$	Sulphuret of ethyle .	$C_4H_5, S.$

The oxide of ethyle, C_4H_5O, is the compound known as *sulphuric ether*.

The common radical, C_4H_5, of these compounds has received the name *ethyle*.

3°. Alcohol distilled with the oxacids or the organic acids, produces a series of compound ethers, formed by the combination of sulphuric ether, C_4H_5O, with the acid employed. Thus, nitric acid, by its reaction on alcohol, gives nitric ether, C_4H_5O, NO_5; oxalic acid, oxalic ether, C_4H_5O, C_2O_3; and so on. This class of ethers may be compared to salts, in which ether plays the part of base.

4°. The strong acids, by their action on alcohol, also produce a series of acid compounds, which are called *vinic acids*, and which may be considered as acid ethers, formed by the combination of 1 equivalent of ether, C_4H_5O, with 2 of the acid. Thus, alcohol and sulphuric acid produce sulpho-vinic acid, C_4H_5O, $(SO_3)_2$, HO.

845. ALCOHOL, properly so called, proceeding from the distillation of fermented liquors, is always diluted more or less with water, of which it may be divested by the absorption of bodies, such as quicklime, and successive distillations. Carbonate of potash, being quite insoluble in alcohol, may be applied to the dehydration of that liquid without distillation.

Alcohol is a colourless liquid of great fluidity and burning caustic taste. When concentrated it is poisonous. Its injection into the veins produces immediate death, probably by the coagulation of the albumen of the blood. Its SG = 0·794 at temperature 60°. It boils at 173°, and has not been congealed by any attainable cold. The density of its vapour is 1·6133. It is soluble in water in all proportions, and is highly inflammable. When concentrated its flame is yellowish, and when weak bluish.

Its vapour transmitted through a porcelain tube at a red heat gave carbon, carburetted hydrogen gases, aldehyde, naphthaline, benzine, and phenic acid.

The centesimal composition of alcohol is—

Carbon	52·57
Hydrogen	12·99
Oxygen	34·44
	100·00

In the presence of oxygen, and under the influence of platinum black or ferments, it is transformed into acetic acid. This change may be thus expressed :—

$$C_4H_6O_2 + 4O = \underbrace{C_4H_4O_4}_{\text{Acetic acid.}} + 2HO.$$

Oxygen is more easily dissolved in alcohol than in water. A mixture of oxygen and alcoholic vapour explodes by the electric spark.

Chlorine and bromine act similarly on alcohol. They absorb 2 equivalents of hydrogen and produce aldehyde :—

$$C_4H_6O_2 + 2Cl = \underbrace{C_4H_4O_2}_{\text{Aldehyde.}} + 2HCl.$$

If the chlorine be present in excess, a compound called *chloral* is produced :—

$$C_4H_6O_2 + 8Cl = \underbrace{C_4HCl_3O_2}_{\text{Chloral.}} + 5HCl.$$

846. The hydrates of potash and soda are readily soluble in alcohol, but after a time transform it into a brown resinous substance. A solution of potash in alcohol is a powerful agent of reduction. Liebig obtained platinum black by the reaction of a mixture of alcohol and potash on the protochloride of platinum.

Alcohol is rapidly oxidised, and even inflamed by the acids which readily give up their oxygen, such as permanganic, chromic, nitric, chloric, bromic, and so on.

847. Certain salts are capable of being distinguished by the colour which they impart to the flame of alcohol. Thus, the salts of strontian give it a *crimson* colour, those of lime *red*, those of copper *green*, and so on.

848. Alcohol manifests a certain affinity for water. Mixture of the two liquids is attended with a sensible elevation of temperature and diminution of volume. Alcohol absorbs humidity from the air, and organic bodies immersed in it give up to it the water they have imbibed, and are thus preserved from putrefaction.

The decrease of volume produced by a mixture of water with alcohol is greatest when 53,939 parts of anhydrous alcohol are mixed with 49,836 parts of water. The sum of these volumes is 103,775, while the volume of the mixture is only 100,000. The mixture has SG = 0·927. In this state of hydration the composition of the liquid is $C_4H_6O_2$, 6HO.

849. Alcohol at 32° mixed with snow reduces the temperature from 32° to −34°·6′, that is, 66°·6′ below the temperature of melting ice.

850. Alcohol is an extensively applicable solvent. It dissolves sulphur, phosphorus, bromine, iodine, the hydrates of potash and soda, the alkaline sulphurets, and such of the chlorides, bromides, and iodides as are soluble in water ; also most of the deliquescent salts, except the carbonate of potash.

851. When a salt, such as carbonate of potash—which, while it is completely soluble in water, is altogether insoluble in alcohol—is added to a mixture of water and alcohol, the alcohol will separate itself from the aqueous solution of the salt and will settle in a stratum on the surface, just as oil will float on water.

852. The chlorides of calcium, zinc, manganese, iron, and magnesium, the nitrates of magnesia and lime, and some other salts, separate from their alcoholic solutions, retaining the alcohol, which in that case plays the part of water of crystallisation.

In organic chemistry alcohol is used to dissolve the resins and the alkaloids, and to purify the acid fats. It opposes the action of certain acids upon the bases, as has been shown by Chevreul. Alcoholised acids in general act upon bases only when the salt they would form is soluble in alcohol.

The presence of alcohol also prevents the strongest acids from acting on litmus.

853. All the varieties of ardent spirits, such as brandy, rum, whisky, and so on, are merely mixtures of alcohol and water, deriving their characteristic

flavour from essential volatile oils originated in the process of fermentation. Brandies are produced from the fermentation of the grape, rum from that of sugar, whisky from that of grain, and so on.

The richness or strength of a spirit is determined by the proportion of absolute alcohol it contains, which is ascertained practically by hydrometric instruments of different forms, some of which show the volume of a given weight, and others the weight of a given volume, at a given temperature.

The best French brandies contain more than 50 per cent of water, and are highly charged with the fragrant essential oil of the husk of the grape. To diminish the cost of transport, they are often highly rectified at the place of production, and then reduced in strength at the place of sale by a little highly flavoured brandy and water; but the result is not equal in flavour to the spirit of like strength immediately distilled from Cognac wine.

Proof spirit contains about 50 per cent of absolute alcohol.

The commercial value of a spirit does not depend alone on its strength. It also depends on its growth, and especially on its age.

854. ALDEHYDE is alcohol deprived of 2 equivalents of its hydrogen, its composition being therefore $C_4H_4O_2$. It is produced in many chemical processes as in the preparation of nitrous ether, fulminating mercury, and so on. It is liquid, colourless, very limpid, with an ethereal and suffocating odour. Its SG = 0·790. It boils at 70°. It is soluble in all proportions in water, alcohol, and ether. It is combustible and burns with a pale flame. It dissolves phosphorus, sulphur, and iodine. Chlorine and bromine transform it into *chloral* and *bromal*. By contact with alkalies it is changed into a brown resinous substance.

It has a strong affinity for oxygen, and reduces several metallic salts. It instantly decomposes nitrate of silver, the metallic base being precipitated, and covers the inner surface of the vessel in which the reaction takes place, with a metallic coating.

It absorbs 1 equivalent of oxygen, and is converted into acetous acid—

$$C_4H_4O_2 + O = C_4H_3O_2, HO.$$

This is sometimes called *aldehydic acid.*

It appears that alcohol submitted to oxidising agents produces the following compounds:—

Alcohol	$C_4H_6O_2$.	Acetous acid . .	$C_4H_4O_3$.
Aldehyde	$C_4H_4O_2$.	Acetic acid . . .	$C_4H_4O_4$.

855. ETHER, commonly called sulphuric ether, because its most convenient mode of preparation is by the action of concentrated sulphuric acid and alcohol, under the influence of heat, is as already stated, alcohol minus 1 equivalent of water :—

$$C_4H_6O_2 - HO = \overbrace{C_4H_5O}^{\text{Ether.}}.$$

Ether is a colourless liquid of great fluidity and a burning taste. It is absolutely neutral. Its SG = 0·7237 at the tem-

perature of 53·6°. It has strong refracting power, is a non-conductor of electricity, and boils at 95·5°.

The cold produced by its evaporation causes a depression of temperature many degrees below that of melting ice. It may be congealed by an intense artificial cold. The density of its vapour is 2·565, two volumes representing an equivalent of ether. Its vapour is heavy, and it often happens that when it falls upon inflamed bodies or incandescent charcoal it takes fire and causes serious accidents.

It burns with a fine white smoky flame, much more luminous than that of alcohol.

Mixed with oxygen or air its vapour is detonating. It is dissolved by 10 parts of water, and in all proportions by alcohol.

856. In commerce ether is sometimes adulterated with alcohol. This may be detected by mixing the ether with a small quantity of water in a graduated tube, by which the alcohol will be dissolved, so as to diminish the volume of the impure liquid in a much greater proportion than if it were pure.

At common temperatures oxygen slowly acidifies ether. The acidification is, however, much accelerated by heat. If a fine platinum wire be suspended over a lamp which contains ether, the wire will become incandescent. A *flameless lamp* is thus produced. In this case the wire, by its presence alone, determines the oxidation of the ether, and this chemical action developes heat enough to render the wire incandescent. In this case acetic acid, aldehyde, and aldehydic acid are formed.

Ether may be decomposed and resolved into carburets of hydrogen and aldehyde, by transmission through a porcelain tube at a red heat.

Ether dissolves 1 part of sulphur in 37, and 1 part of phosphorus in 80. It dissolves iodine and bromine easily. It absorbs ammoniacal gas, and dissolves some metallic chlorides, as those of zinc, mercury, and gold. Kuhlman obtained a crystalline compound of ether and the perchloride of iron.

As a solvent ether is of great value in immediate analyses, serving for the preparation of a great number of organic bases, for the purification of fat bodies, for the dissolution of caoutchouc, and other purposes.

It is employed in medicine as an antispasmodic and an anæsthetic. Applied to the forehead it produces coolness, which assuages headache. One of its most important medical applications consists in its anæsthetic virtue, by which a patient is rendered insensible to pain under surgical operations. In this respect, however, it has been superseded by chloroform.

857. ETHERS IN GENERAL comprise a class of compounds, produced by the reaction of the acids, whether mineral or organic, upon alcohol, by which a certain number of equivalents of water are separated from the latter.

They are formed under various conditions, according as the acid is strong or weak, free or combined. They are also produced in certain cases by the reaction of the chlorides, iodides, and bromides.

A strong acid heated with alcohol in a distilling apparatus gives a corresponding ether. Oxalic, hydrochloric, acetic, and butyric ethers are thus obtained.

Ethers are obtained from weak acids, such as benzoic acid, by mixing them with a strong acid, such as sulphuric or hydrochloric, and distilling with alcohol.

858. The vinic acids in general are prepared by mixing an excess of acid with alcohol, saturating with lime, and then decomposing the salt of lime. Sulphovinic and phosphovinic acids are examples of this process.

A neutral ether partially decomposed by potash gives a vinic salt, which is then treated by hydrofluosilicic acid. Oxalovinic acid is prepared in this way.

859. Ethers are sometimes found naturally formed in certain vegetables. Thus the salicylic ether of methyle constitutes the essential principle of the *Winter green*, supplied by the *Gaultheria procumbens*, a plant of the family of *Ericinea* found in New Jersey, U.S. Cinnamic ether is distilled from the balsam of Peru. The nitrous ether of methyle is obtained by the reaction of nitric acid on brucine.

The compound ethers produce alcohol under the long-continued influence of hydrated alkalies, and sometimes even by the mere action of water, while their acid constituent combines with the alkali or the water.

An excess of ammonia decomposes ethers, producing alcohols and amides. Oxalic ether in an aqueous solution of ammonia yields alcohol and oxamide. When the ether is in excess compounds called *amethanes* are formed, which may be considered as amides of vinic acids.

860. VINIC ACIDS in general are combinations of the acids with ordinary ether. Thus:—

$$C_4H_5O + 2(SO_3) + HO = \overbrace{C_4H_5O, (SO_3)_2, HO.}^{\text{Sulphovinic acid.}}$$

$$C_4H_5O + PO_5 + 2HO = \overbrace{C_4H_5O, PO_5, 2HO.}^{\text{Phosphovinic acid.}}$$

861. HYDROCHLORIC ETHER results from the direct action of hydrochloric acid on sulphuric ether—

$$\overbrace{C_4H_5O}^{\text{Sulphuric ether.}} + HCl = \overbrace{C_4H_5Cl}^{\text{Hydrochloric ether.}} + HO.$$

This ether is liquid, colourless, soluble in 24 parts of water: its SG=0·874 at 41°. It boils at 52°. By its evaporation an intense cold is produced. It is decomposed at a red heat, producing equal volumes of carburetted hydrogen and hydrochloric acid. It does not precipitate nitrate of silver. It burns with a green smoky flame, producing an acid liquor in which the pre-

sence of hydrochloric acid is easily detected. It has great stability and can be distilled from potash without sensible alteration.

862. NITRIC ETHER, C_4H_5O, NO_5 is liquid, of a sweet odour and saccharine taste. It is insoluble in water. Its SG = 1·112 at 62·5°. It boils at 185°. At a high temperature it detonates violently, and is decomposed by an alcoholic solution of potash, giving nitrates, and producing alcohol.

863. NITROUS ETHER, C_4H_5O, NO_3, has the odour of rennet pippins. It is rarely pure, generally containing aldehyde. It boils at 70°. Its SG = 0·886.

864. OXALIC ETHER, C_4H_5O, C_2O_3, is liquid, colourless, oleaginous, and SG = 1·0229. It boils at 360°. Its odour is aromatic. It can be preserved a certain time in contact with water, when pure. Potash decomposes it.

$$2(C_4H_5O, C_2O_3) + KO = \overbrace{KO, C_4H_5O, 2(C_2O_3)}^{\text{Oxalovinate of potash.}} + \overbrace{C_2H_6O_2}^{\text{Alcohol.}}.$$

865. ACETIC ETHER, $C_4H_5O, C_4H_3O_3$, is liquid, colourless, with an agreeable odour. It burns with a yellow flame. Its SG = 0·89 at 59°. It is dissolved by seven times its volume of water. The hydrated alkalies speedily change it into acetic acid and alcohol. It is soluble in all proportions in alcohol, wood-spirit and ether. It boils at 165°. The density of its vapour is 3·067. It dissolves the resins, essential oils, and generally all substances which are soluble in common ether.

Perchlorinated acetic ether, produced by the continued action of chlorine, which expels all the hydrogen from acetic ether, has the composition $C_4Cl_5O, C_4Cl_3O_3$. This is an oily liquid which boils at 473°, and is transformed into chloracetates under the influence of the alkalies.

866. FORMIC ETHER, C_4H_5O, C_2HO_3, is a colourless liquid of great fluidity, with an agreeable pungent odour. SG = 0·915 at 64·5°. It boils at 128°, is soluble in 10 parts of water, and in all proportions in alcohol and the ethers.

CHAPTER XXVI.

WINE.—WOOD-SPIRIT.—CHLOROFORM.

867. WINE is the fermented juice of the grape. This juice when first expressed has a saccharine savour, which it soon loses, becoming acid and alcoholic.

All sorts of grape are not equally suited for the production of wine. The Chasselas grape of Fontainebleau, so delicious an article of dessert, is quite incapable of yielding potable wine. Grapes, fit for the production of wine, should be ripened in a position which will insure to them a warm, constant, and regular temperature. The soil should have a mixed character, partly silicious and partly argillaceous. Old vines, cæteris paribus, give better wine than younger ones.

Many constituents are involved in the composition of the grape, all of which affect directly or indirectly the quality of the wine it produces. These are principally, water, glucose or grape sugar, pectic acid, tannin, albumen, a peculiar ferment which produces the spon-

taneous alcoholic fermentation of the glucose; several nitrogenous compounds soluble in water and alcohol; essential oils; colouring compounds blue, red, and yellow; which being differently durable cause the colour of the wine to vary with time from violet to red orange and tawny yellow, fatty compounds, one of which forms œnanthic ether, which imparts to the wine its peculiar *bouquet;* pectates and pectinates of lime, soda and potash; tartrates and paratartrates of potash, lime and alumina; chlorides of potassium and sodium, phosphate of lime, oxide of iron and silica.

868. The quality of wine depends much on the condition under which the vintage takes place. The fruit should be fully ripe, the weather dry and cloudless. The grapes collected in baskets are transferred to barrels or troughs, in which they are first pressed by rakes or trodden by men's feet, but this must not be done subject to a high temperature, since in that case premature fermentation would ensue.

If it be desired to make white wine, the pulp is immediately submitted to the wine press. If, on the contrary, red wine be desired, the pulp is left to itself for several days, so that fermentation may commence, and that the liquor may dissolve the colouring matter and tannin contained in the skin and stalks. In the fabrication of wines of the finer sorts the grapes are picked and the coarser parts of the stalks removed, especially in seasons when the bunches are less rich in fruit. The troughs in which the first fermentation takes place are left open for the free escape of the carbonic acid. The duration of this process varies with the temperature of the weather and the nature of the grape. It is considered to be terminated when the evolution of gas ceases, and when the wine has acquired a suitable colour. In the ordinary wines its duration varies from 3 to 8 days, but it sometimes continues from 4 to 6 weeks.

When the fermentation has ceased the clear liquor is discharged by a cock provided for the purpose, and the marc mixed with a small quantity of water is again submitted to the press, by which a weak wine is obtained which easily sours.

The wine is then transferred into barrels, which, for a certain time, are left open to allow the escape of the carbonic acid evolved in the process of fermentation, which has not as yet altogether ceased. When it has ceased the wine is again drawn off, and towards the months of March and April it undergoes the process of *clearing*, which is effected by the white of egg, ox's blood, or gelatine. These substances enter into combination with the tannin, with part of the colouring matter, and in their coagulation carry away the matters which, being held in suspension, render the wine turbid.

869. *Sparkling wines*, such as champagne, are prepared from the black grapes of the best quality, the juice of which is sweeter than that of the white grape. The fruit collected in warm weather is carefully transferred to the wine-press, where, by a gentle pressure, the first portions of juice are extracted without tearing or bruising the skin or stalks, which would impart a colour to the liquor. This gives wine of the first quality. The marc is then submitted to a more severe pressure, giving a juice by which a pinkish-coloured wine is obtained of less esteemed quality. A third or fourth repetition of this process gives inferior wines, which are usually mixed with common red wines to flavour them.

The liquors thus produced are then left to a tumultuous fermentation in large barrels, where they disembarrass themselves of a great quantity of their ferment, which collects in froth at the surface. After about 24 hours the liquor

is drawn off into other barrels, which are nearly filled and imperfectly closed, so as to leave openings for the escape of the carbonic acid which still continues to be evolved. A month later the liquor is drawn off and cleared. The same process is again twice repeated, at intervals of a month, until, at length, the wine is bottled, in which process from 3 to 5 per cent. of sugar-candy, dissolved in its own weight of water, is added to it. The bottles are corked and wired with the greatest care, and laid in rows upon their sides. A part of the sugar-candy undergoes alcoholic fermentation under the influence of the ferment which still exists in the wine; but the carbonic acid evolved in this process not having any means of escape remains in solution in the liquor, and the unfermented part of the sugar-candy imparts to the wine its characteristic sweetness. When the bottles are uncorked the carbonic acid, which is thus dissolved in the wine, being released from the confining pressure, escapes, rising in bubbles through the liquor, and produces the sparkling and foaming effects which are familiar to champagne drinkers.

870. According to Gay Lussac, wine in general is a liquid the mean composition of which is 8 to 10 parts of alcohol, 85 to 90 of water, and 2 to 5 colouring and extractive matter, tartar, and other salts of alumina, lime, &c., a ferment, and sometimes sugar which has not been decomposed by fermentation.

Alcohol is its essential principle, the proportion of which varies from 7 to 17 per cent. of its volume, according to climate, soil, culture, and, above all, the temperature in which the grape is ripened. The wines of the South are stronger than those of the North, and those proceeding from the same vineyards vary in strength from vintage to vintage. Sparkling wines contain a large quantity of carbonic acid gas, (CO_2), to the escape of which their effervescence is due.

871. WOOD-SPIRIT, *pyroligneous ether*, or *pyroxylic spirit*, $C_2H_4O_2$, obtained by the distillation of wood, is a colourless liquid of alcoholic odour and burning taste, highly inflammable, and neutral to the colour tests. Its SG = 0·82074 at 68°. It is soluble in all proportions in water, alcohol, and ether. It boils at 150°. The density of its vapour is 1·620.

Its composition is differently viewed by different chemists, either as a bihydrate of methylene, or an hydrate of the oxide of methyle :—

$$C_2H_4O_2 = \overbrace{C_2H_2}^{\text{Methylene.}}, 2(HO) = \overbrace{C_2H_3O}^{\text{Oxide of methyle.}}, HO.$$

Treated with acids wood-spirit gives: 1°, methylic ether, C_2H_3O; 2°, methylic acids, which correspond to the vinic acids; 3°, a series of ethers, in which the oxygen of methylic ether is replaced by an equivalent of a metalloid (this series is produced by the hydracids; an example of this class is the hydrochloric ether of methylene, C_2H_3Cl); and 4°, ethers formed by the combination of oxacids and organic acids with methylic ether, represented by the general formula, C_2H_3O, A.

872. CHLOROFORM, C_2HCl_3, is prepared by various methods, and has acquired great importance since it has superseded ether as an agent for producing insensibility in surgical operations.

It may be prepared by the action of alcohol or acetone on hypochlorite of lime, or by decomposing hydrated chloral by a solution of potash:—

$$C_4HCl_3O_2, HO + KO = C_2HCl_3 + KO, C_2HO_3;$$

and also by treating the chloracetates with an excess of hydrated alkali: —

$$\underbrace{KO, C_4Cl_3O_3}_{\text{Chloracetate of potash.}} + KO, HO = 2(KO, CO_2) + \underbrace{C_2HCl_3}_{\text{Chloroform.}}.$$

Chloroform is a colourless liquid, of an agreeable etherial odour and sweetish taste. Its SG = 1·48 at 65°. It boils at 141°, the density of its vapour being 4·2. It burns with a green flame. When transmitted through an incandescent tube it is decomposed, being resolved into carbon, hydrochloric acid, and a body crystallised in long white needles. It is insoluble in water, but highly soluble in alcohol. Neither potassium nor sulphuric acid have any action upon it. Under the influence of direct solar light it is converted into the chloride of carbon. The alkalies easily convert it into formiates and chlorides; a reaction which may be regarded as characteristic.

CHAPTER XXVII.

ESSENTIAL OILS.—RESINS.—VARNISH.—CAOUTCHOUC.

873. ESSENTIAL OILS is the general name given to volatile oily products obtained from aromatic vegetables.

In many cases these oils exist already formed in vegetables. Thus, every one is familiar with the volatile and inflammable oil which is expelled by compression from the rind of an orange or lemon. In other cases, however, they do not exist immediately in the plant, and are only formed by its contact with water. The oils of almonds and mustard are examples of this.

Such essences are extracted by various expedients, but most frequently by distillation. When they exist in great abundance, they are extracted by compression. Thus obtained, however, they are rarely pure, holding generally in solution solid bodies, called *stearoptenes*. They are generally yellow, and assume a deeper tint by exposure to the air. Their boiling point varies from 280° to 400°. Although volatile they are often decomposed by ebullition. They vary in SG, some being lighter, others heavier than water, the former being also the more volatile. If thrown upon paper they produce the same effect as oil or grease, rendering it translucent, but when the paper is warmed, this disappears.

Water dissolves some essential oils, producing aromatic or scented waters. Most of them are soluble in alcohol, ether, and the fat oils.

874. THE VOLATILE OILS slowly absorb oxygen, and are transformed into resins or acids. Some produce acetic acid. They also dissolve sulphur and phosphorus, and deposit these bodies by evaporation in crystals. Chlorine,

bromine, and iodine, act upon them, forming compounds by substitution, and producing at the same time, hydrochloric, hydrobromic, and hydriodic acids.

Nitric acid exercises generally a strong reaction on the essential oils, producing sometimes their inflammation, and also acting like oxygen in forming resins and organic acids.

They often absorb hydrochloric acid, producing crystallised hydrochlorates. A cold and dilute solution of potash has no action on them, but when transmitted over hydrated potash hydrogen is often disengaged, while the oil is oxidated, and transformed into an organic acid, which remains in combination with the potash. Some of them absorb ammonia, forming definite compounds with that base.

They are used in medicine as aromatic principles, and in the arts to produce varnishes, by dissolving the resins. They are also used to efface spots and stains of grease.

875. They may be grouped in three chief divisions: 1°, those which consist of carbon and hydrogen, C_nH_m; 2°, those which also contain oxygen, $C_nH_mO_o$; and, 3°, those which are characterised by the presence of sulphur. Those of the first class are lighter, and those of the two latter generally heavier than water.

The oxygenated oils may be grouped in six classes: 1°, those which present the characters of alcohols; 2°, those which are analogous to aldehydes or hydrides; 3°, solid oils analogous to camphor; 4°, acid oils; 5°, indifferent oils; and, 6°, ethers.

876. Essence of turpentine, $C_{20}H_{16}$, obtained by distillation from the turpentine of the *Pinus maritima*, is a colourless liquid of great fluidity, of a strong balsamic odour and pungent burning taste. Its SG = 0·86. In the crude state it reddens litmus, but is neutral when rectified. It boils at 303°, is inflammable, burning with a smoky flame. Its vapour has a density of 4·764. It is insoluble in water, but very soluble in alcohol and ether. Exposed to the air it absorbs oxygen, and is resinified. It exhibits left-handed polarisation.

It forms with water four hydrates, containing respectively, 1, 2, 4, and 6 equivalents of water.

877. Oil of lemons, $C_{10}H_8$, has a close analogy in composition and properties to oil of turpentine. It is obtained from the rind of lemon by compression, and is purified by distillation. When rectified, it is transparent and colourless. By distillation it is resolved into two oils, apparently different; one of which boils at 320°, and the other at 347°. It exhibits right-handed polarisation.

878. Oil of bitter almonds, $C_{14}H_6O_2$, obtained by macerating bitter almonds and distilling them with water, is a colourless transparent liquid, having a strong refracting power. Its odour resembles that of hydrocyanic (prussic) acid; it acts powerfully on the animal economy, being highly poisonous. Its taste is burning, and its SG = 1·053. It boils at 356°. It is soluble in 30 parts of water, is very inflammable, and burns with a smoky

flame. Exposed to the air, or under the influence of an oxidating body, it absorbs 2 equivalents of oxygen, and is converted into benzoic acid :—

$$C_{14}H_6O_2 + 2O = \underbrace{C_{14}H_5O_3, HO}_{\text{Benzoic acid.}}.$$

Chlorine disengages hydrochloric acid, and produces chloride of benzoyle.

$$C_{14}H_6O_2 + 2Cl = \underbrace{C_{14}H_5O_2Cl}_{\substack{\text{Chloride of}\\ \text{benzoyle.}}} + HCl.$$

879. CAMPHORS. Concrete volatile oils are found in certain vegetables, which are very similar in their properties to the solid and volatile oil obtained from the *Laurus camphora*, and have hence received the general name of *camphors*. Submitted to the influence of anhydrous phosphoric acid they lose water, and produce a carburet of hydrogen, which has a certain analogy to the essence of turpentine.

880. CAMPHOR, $C_{20}H_{16}O_2$, is a white brittle solid of burning taste and characteristic odour. It crystallises in octohedrons, and when moistened with alcohol can be easily pulverised. Its SG = 0·996. It melts at 347°, and boils at 400°. The density of its vapour is 3·317. It is combustible, and burns like the essential oils. It is almost insoluble in water, but very soluble in alcohol and ether.

881. SULPHURETTED ESSENTIAL OILS. Among the oils into which sulphur enters as a constituent are those of black mustard, horse-radish, cochlearia (scurvy-grass), hops, assafœtida, and garlick.

882. THE OIL OF MUSTARD, $C_8H_5NS_2$, obtained from the seeds of the *Sinapis nigra*, is a colourless transparent liquid, with SG = 1·010 at 60°. Its odour is pungent and disagreeable. It disorganises the skin. It boils at 290°. The density of its vapour is 3·50. When warm it dissolves sulphur and phosphorus, which crystallise on cooling. In contact with liquid ammonia it forms a crystalline compound called *thiosinnamine*, which has the characters of an organic base :—

$$C_8H_5NS_2 + NH_3 = C_8H_8N_2S_2.$$

883. RESINS are a class of organic compounds which have great importance owing to their numerous applications in the industrial arts. They abound in the vegetable world, but their chemical analysis and properties have not yet been fully investigated. They are usually extracted, together with essential oils, from trees, by incisions made in them, the oils being afterwards separated from the resins by distillation.

Resins are often solid and translucent; rarely colourless. Some are heavier than water. They develope negative electricity by friction, and are non-conductors. They are all insoluble in water, but generally soluble in alcohol. Their alcoholic solution when mixed with water becomes milky and turbid, the resin being precipitated. Some—copal, for example—are insoluble also in alcohol. Most are soluble in ether. A few—the resin of jalap, for example—are exceptions to this. They are all dissolved by the oils fixed and volatile.

With some exceptions, they are uncrystallisable. They soften by heat, fuse, and by distillation are resolved into solid liquid and gaseous carburets of hydrogen, phenic acid, and other compounds.

They are combustible, burning with an obscure smoky flame, and leaving a carbonaceous deposit. Oxygen generally has no action upon them. The resin of guiacum, however, when exposed to the air becomes blue.

The alkalies often dissolve the resins, acting in this case like weak acids. Nitric acid strongly oxidises them.

The resins are classed by Unverdorben (who has made them the subject of extensive researches) as *positive* and *negative*, the negative being those which show an acid reaction by reddening vegetable colours and combining with bases, the positive or indifferent being those which do not manifest this property.

The compounds formed with bases by the negative resins are called *resinates*, and also, though less properly, *soaps of resin*. These compounds like common soaps form a lather with water, but are not precipitated by sea salt.

884. COLOPHONY is the resin obtained from turpentine. This latter substance extracted by incision in the living tree from most of the family of *Coniferæ*, but chiefly from the *Pinus laryx*, is a mixture of the essential oil of turpentine and the resinous compound called colophony; 250lb. of turpentine give about 30lb. of the essence, and 220lb. of colophony.

885. COPAL, one of the most important of the resins of the third class, is obtained from the *Hymen verrucosa*. It is hard, almost colourless, and without taste or odour. Its SG = 1·139. It melts without change, is almost insoluble in anhydrous alcohol, is softened in boiling alcohol, and is, in fine, dissolved under the influence of alcoholic vapour. It first swells in ether, and is then dissolved. It is almost insoluble in the alkalies.

When bruised and kept for a month in a stove it absorbs oxygen from the air, loses carbon, and becomes very soluble in ether and even in alcohol. This property has supplied the means of preparing certain varnishes.

886. LAC exudes from several trees in India through holes made by the female of a hemipterous insect called the *Coccus lacca*. It is this insect which imparts to lac its characteristic red colour. It is of very complex composition, containing five different resins.

It is found in commerce in two states called *stick lac* and *shellac*, the latter resulting from the fusion of the former.

Lac has several important uses in the arts. It is used as a cement for earthenware and porcelain; also in the fabrication of sealing-wax, which consists usually of 40 shellac, 12 of turpentine, 1 of balsam of Peru, and 36 of vermilion.

887. AMBER is considered to be a fossil resin. Its fracture is conchoidal, its colour varies from yellow to brown; its SG = 1·081. It melts at 548°. It is inflammable, and in burning diffuses an agreeable odour and leaves a carbonaceous residuum. It is insoluble in water, and but slightly so in alcohol or ether, which do not dissolve more than 10 or 12 per cent. of it. After being fused, however, it becomes completely soluble in alcohol, and it may thus be rendered available for varnishes.

It is decomposed by distillation, giving several liquid carburets of hydrogen, the boiling points of which vary from 284° to 374°. These are isomeric with the essence of turpentine. An acid compound called *succinic acid* also results from the distillation.

According to Reich, amber distilled with a concentrated solution of caustic potash produces a crystalline sublimate identical with common camphor. Dœpping had previously ascertained that amber treated with nitric acid produces camphor.

888. BALSAMS are of two classes: 1°, those which contain benzoic acid; and 2°, those which contain cinnamic acid. Exposed in air they gradually thicken, and at length are completely solidified. They are regarded as mixtures of essential oil, different resinous substances, and either cinnamic or benzoic acid. It is considered probable that a balsam before it is altered by exposure to air is a liquid which contains neither resin nor either of the acids.

Benzoin is a balsam of pure benzoic acid. Liquid Peru balsam contains only cinnamic acid. There are certain balsams which include both acids.

889. VARNISHES are solutions of resinous matter intended to be spread over a surface so as to give it a shining, transparent, and hard coating, capable of resisting the influence of air and moisture. Such a coat consists of the resinous constituents of the solution which remain upon the surface after the liquid solvent has evaporated.

The following are the principal materials of varnish:—

SOLVENTS.	RESINS.	COLOURING MATTER.
Poppy oil.	Copal.	Gamboge.
Linseed oil.	Amber.	Dragon's blood.
Walnut oil.	Mastic.	Aloes.
Essence of turpentine.	Sandarac.	Saffron.
Essence of spike-lavender.	Lac.	
Alcohol.	Elemi.	
Ether.	Benzoin.	
Wood-spirit.	Colophony.	
Acetone.	Common resin.	
Benzole.	Caoutchouc.	

The following are the qualities characteristic of good varnishes: 1°, after drying they should retain their brilliancy without presenting a dull or greasy appearance; 2°, they should adhere closely to the surface without scaling or cracking; 3°, they ought to dry as rapidly as possible, and should retain their hardness undiminished.

Varnishes in which the solvent of the resin is a fat drying oil are usually made with copal or amber.

Spirit varnishes are susceptible of polish, but have less solidity than those made with the essences. The alcohol evaporates more rapidly than the essence, and leaving a residuum consisting of the pure resinous matter which it held in solution, while the essence of turpentine being oxidated by contact with air, forms a resinous coating, which renders the resin in solution more fixed. The essence of turpentine alone applied upon a surface constitutes a sort of varnish. The dryness of spirit varnishes is often corrected by the addition of a certain proportion of oily matter, or even of the soft resins.

890. Caoutchouc, C_8H_7, which has acquired considerable importance from its numerous applications, is obtained from a milky juice which exudes from a great number of plants, but for the purposes of commerce it is extracted chiefly from the *Siphonia cahuca*, also called *Hevea guianensis*, a plant which grows in South America and Java. The tree has transverse incisions made in its bark, from which the milky juice flows, and is received on pear-shaped moulds of clay, on which it forms a thick coat, which is dried and hardened either in the sun, or with the smoke of a fire; it thus becomes blackened. The clay being crumbled and thrown out the caoutchouc or *india-rubber* remains in the form of an empty pear-shaped bottle.

The natural milky juice itself has been lately imported.

Caoutchouc when pure is transparent and colourless. Its surfaces when freshly cut readily cohere; a property which facilitates its application to the formation of flexible tubes.

Concentrated sulphuric and nitric acids decompose it, but it resists all the other acids, and even chlorine as well as potash in concentrated solution. It is a non-conductor of electricity. Its SG=0·925. Exposed to the temperature of 32° it is rendered hard and loses its characteristic pliability and elasticity, but recovers these qualities when warmed. It is insoluble in water, but soluble in pure ether, from which it is precipitated by alcohol. In contact with cold oil of petroleum it dilates in volume, and is completely dissolved if boiled. It is also soluble in several empyreumatic oils, in the essential oils, the fat oils, and the sulphuret of carbon. It is fusible at 248° producing an oily substance. In this process it seems to undergo an isomeric change.

891. Water and air-proof tissues are usually prepared by spreading a very thin coat of caoutchouc dissolved in the pure essence of turpentine, over the surface of a stuff upon which a second similar fabric is applied, so that the two cloths are pasted together by the intermediate coating of caoutchouc. The solution used for this purpose should be in a pasty state so as not to penetrate or stain the stuff.

Caoutchouc enters into the composition of *marine glue*, a mixture remarkable for the strong adhesion it produces when applied between surfaces of wood. It consists of a solution of caoutchouc in the essential oil of tar, to which gum-lac is added. It is employed at a temperature of about 250° for the construction of compound masts, and for repairing damage done to the rigging of vessels at sea.

It is largely used in the preparation of elastic and impermeable tubes, and other pieces in surgical apparatus; but its most extensive application in the arts

consists in the production of water-proof cloth for outside coats, and braces, bands, and other articles which require great elasticity.

The solvents commonly employed for the dissolution of caoutchouc are ether, sulphuret of carbon, oil of tar, and several carburets of hydrogen, and more especially those which proceed from the distillation of caoutchouc itself. The liquid most commonly employed is well rectified essence of turpentine.

892. Caoutchouc combines directly with sulphur, which renders its elasticity permanent at common temperatures. This process, called *vulcanisation*, can be effected by various other methods, the most simple of which consists in immersing caoutchouc in a mixture of 100 parts of sulphuret of carbon, and 2·5 of the chloride of sulphur. After an interval of a minute or two the caoutchouc is withdrawn and stove-dried in a current of air at the temperature of 70° to 80°; after another immersion, and another similar dessication, the caoutchouc is washed first in a weak alkaline solution, and then in water.

893. GUTTA PERCHA, a substance more recently imported from Borneo, bears a close analogy to caoutchouc. It is whitish, hard, coriaceous, and flexible. It becomes soft and elastic when heated. It may be softened so as to be kneaded in boiling water. Its SG = 0·979. When distilled it yields inflammable oils. It is insoluble in water and alcohol, and soluble in sulphuret of carbon. Ether first swells it, and then slowly dissolves it. It resists the action of alkaline solutions and hydrochloric acid. Sulphuric acid when concentrated carbonises it with difficulty. Nitric acid transforms it into a yellow resinous substance.

After it has been disembarrassed of the foreign matters which it always contains, such as certain resins and a peculiar acid, its composition is found to be nearly identical with that of caoutchouc. It may therefore be considered as a carburet of hydrogen.

894. It is used in the arts to make riding-whips, coach-whip handles, bands for the transmission of motion in machinery, bougies and other apparatus in surgery. It is also used to surround and protect the conducting wires of electric telegraphs when they are buried in the earth or sunk in the sea, being adapted for this purpose by reason of being a non-conductor of electricity.

CHAPTER XXVIII.

FATS.—OILS.—WAX.

895. FATS are organic compounds of vegetable or animal origin, sometimes liquid, sometimes solid, but always easy of fusion, and which when liquid leave a durable spot upon paper which renders it more or less translucent, an effect with which every one is familiar when oil or melted tallow is applied to paper.

896. It has been ascertained that the familiar fat substances such as oil, butter, grease and tallow are, with very few exceptions, mixtures of organic compounds or immediate principles called

stearine, *margarine*, *oleine*, *butyrine*, *caprine*, *caproine* and *phocenine*, and that these are resolved under the influence of the alkalies into *glycerine*, the name given to the essential principle of the oils, and peculiar fat acids, which take their names from the compounds of which they form a constituent. Thus *stearine*, consists of glycerine and *stearic acid*, *oleine* of glycerine and *oleic acid*, and so on.

897. STEARINE, $C_{71}H_{70}O_8$, exists in almost all the solid fats, and in several vegetable oils. Its proportion is in general so much the more considerable as their consistency is greater, and their point of fusion more elevated.

If mutton suet be heated with 8 or 10 times its volume of ether or essence of turpentine, the margarine and oleine will remain in solution, and the stearine will be precipitated in pearly crystals.

Stearine is white, very combustible, without taste or odour, and fusible at 144°. It is insoluble in water, and soluble in about 7 times its weight of boiling alcohol, from which, however, it is precipitated on cooling. It is more soluble in boiling ether, which however holds but little in solution when cold.

898. MARGARINE is found with oleine and stearine in most fats, and more especially in human fat. It is separated by boiling with alcohol. It has a general resemblance to stearine, but fuses at 116°. It is saponified by the alkalies, and resolved into glycerine, and margaric acid.

899. OLEINE exists in all fatty substances, but in a much larger proportion in the oils than in the solid fats, a circumstance from which it takes its name. It is yellowish, but is discoloured by direct solar light. It continues liquid at 32°. It absorbs oxygen from the air, disengaging carbonic acid, and is thus partially resinified. It is by this property of oleine that the change which oils undergo after a time, by exposure, is explained.

It is insoluble in water, sparingly so in cold alcohol, but is soluble in all proportions in ether.

By the alkalies it is saponified, and resolved into glycerine, and oleic acid. Its exact composition has not been ascertained.

900. STEARIC ACID is white, crystallises by fusion in brilliant needles, and is soluble in all proportions in alcohol and ether. Its point of fusion is 158°. It has neither taste nor odour, reddens litmus, is inflammable, and burns with a bright white flame. It is the chief constituent of composition or stearine candles. It is not volatile, and when distilled is resolved into margaric acid, margarone, carbonic acid, and a carburet of hydrogen, isomeric with olefiant gas. Nitric acid transforms it into margaric, succinic, and suberic acids.

It forms with potash two stearates, the bipotassic or normal stearate, $(KO)_2\overline{St}$, and the monopotassic, $KO, HO, \overline{St}$. The former is very soluble in pure water, and has an alkaline reaction.

The neutral stearate of soda, $(NaO)_2\overline{St}$, is analogous to that of potash.

901. MARGARIC ACID, $\overline{Ma}=C_{34}H_{33}O_3$, and the margarates, $MO, \overline{Ma}$, have a remarkable analogy to stearic acid and the stearates, the composition being such, that $2\overline{Ma}$ exceeds $\overline{St}$ by only a single equivalent of oxygen, so that $2\overline{Ma}=$

$\overline{St} + O$. Margaric acid may be prepared by various methods, one of which consists in treating stearic acid by nitric acid at 32° of Beaumé's areometer. It melts at 140°, and when submitted to distillation volatilises with partial decomposition.

902. OLEIC ACID, $\overline{Ol} = C_{36}H_{33}O_3$, derived from the oils which are not drying, and especially from those of almonds and olive, goosegrease and butter, is a colourless, insipid, and inodorous liquid, insoluble in water, very soluble in alcohol, and soluble in all proportions in ether. It dissolves all the solid fats, stearic acid, margaric acid, and so on.

It absorbs oxygen at common temperatures, and more rapidly when heated. It is decomposed by heat, producing sebacic acid, accompanied by the formation of carbonic acid, gaseous and liquid carburets of hydrogen, and two peculiar acids, called *caprylic* and *caproic*.

Oleic acid forms soluble compounds with the alkalies expressed by the general formula $MO, \overline{Ol}$.

903. GLYCERINE, $Gl = C_6H_8O_6$, is liquid, inodorous, colourless, and of a sweetish savour. Its $SG = 2{\cdot}28$. Water and alcohol dissolve it in all proportions. It is almost insoluble in ether. Even the most dilute nitric acid attacks it briskly, producing a deliquescent acid, which soon turns to oxalic and carbonic acids.

Its aqueous solution left for several months, at a temperature of 75° to 85°, in the presence of ferments, suffers a decomposition, in which acetic and metacetonic acids are formed.

904. GENERAL PROPERTIES OF NEUTRAL FATS. The three substances which constitute fat bodies, whether of vegetable or animal origin, are *stearine*, *margarine*, and *oleine*. It may therefore be expected that a close similarity must exist between the animal fats and vegetable oils. The colouring, sapid and odorous principles peculiar to each, have but little influence on their chemical properties.

Heat alone being insufficient to expel the fat principle from vegetable seeds and grains, trituration, pressure, and the agency of water are also resorted to, but the solvents are very rarely employed.

The vegetable oils differ in consistency. Some remain liquid at very low temperatures, some are congealed by winter cold, while others, such as those of palm, cocoa, and chocolate, have the consistency of butter at common temperatures. They are all lighter than water, their SG varying from 0·919 to 0·970.

Air acts differently on them. Some, distinguished as *drying oils*, are rapidly dried, while others called *rancid oils*, are very slowly resinified. In drying they absorb oxygen. In general they consist of margarine, and oleine, either simply mixed or chemically combined.

Oils exposed to air become acid, and acquire a disagreeable odour. They are then said to be *rancid*. In this case they undergo a species of fermentation, due to nitrogenous bodies, which they hold in solution. Heat resolves them into margaric and oleic acids, and glycerine.

Chlorine and bromine produce compounds with them which have not yet been investigated.

905. Olive oil is obtained from the fruit of that name by crushing and pressure. The finest is expressed cold. Inferior qualities are obtained by the agency of heat and fermentation.

It congeals at some degrees above 32°, and easily becomes rancid. Its SG = 0·9192 at 53°.

906. Linseed oil extracted from flax, has a yellowish colour, and faint odour. Its SG = 0·939 at 53°. It congeals at 0° to 5°. It is dissolved by 40 times its weight of cold, and 5 of boiling alcohol, and by 1·6 of ether. It is a rapidly drying oil, and is therefore of much use in the fabrication of varnishes and in oil painting.

Combined with litharge it is used in the preparation of printing ink, black varnishes for leather, in gummed taffeta, and other like articles. The consistency, and in some degree the elasticity of caoutchouc may be imparted to it, and it is thus rendered fit for certain surgical apparatus.

When fresh and cold pressed it forms with soda a soft yellow soap.

907. Castor oil, expressed from the seeds of the *Palma Christi*, or *Ricinus communis*, used so extensively as an aperient, is distinguished from all other oils by its solubility in alcohol, and the peculiar products of its saponification, among which is an acid called *ricinoleic acid*, $C_{36}H_{35}O_5$, HO.

908. Palm oil, expressed from the fruit of a species of palm of Guinea and Senegal, melts at 68°, has an agreeable odour and yellowish colour. It consists chiefly of a neutral substance called *palmitine*, fusible at 122°, mixed with yellow colouring matter, and a ferment by which palmitine is by degrees resolved into glycerine and palmitic acid, $C_{32}H_{31}O_3$, HO. This acid melts at 136°. Distillation slightly alters it. It crystallises in brilliant spangles from alcohol. Chlorine decomposes it, producing hydrochloric acid and several fat acids.

Palm oil is an article of considerable commerce in this country, being extensively employed in the manufacture of soap and candles. After being bleached, palmitine almost pure is obtained from it by a regulated pressure, and of the product candles are made. The remaining constituent is an oil used in the manufacture of soap.

An extensive class of fatty compounds are derived from the animal organism.

909. Human fat is regarded as a mixture of oleine and margarine.

910. Tallow is the fat of herbivora. It is a mixture of stearine, margarine, oleine, and a neutral substance which is found in most abundance in the deer, called *Hircine*. It yields by saponification the corresponding acids, stearic, margaric, oleic, and hircic.

911. BUTTER is of complex composition, consisting of *oleine*, *margarine*, *butyrine*, *caprine*, and *caproine*, which when saponified are converted into the corresponding acids.

Capric, caproic, and butyric acids, are volatile, and can be separated from the others by distillation. The fat liquid obtained from butter by compression is almost exclusively formed of a substance, which is transformed by saponification into glycerine, and an acid called *oleobutyric* acid, the composition of which is $C_{34}H_{30}O_4$, HO.

Fresh butter consists according to Bromeis of—

Margarine	68
Butyroleine	30
Butyrine, caprine, and caproine	2
	100

912. SPERMACETI or CÉTINE, $C_{64}H_{64}O_4$, is one constituent of the fat matter found in the cellular tissue, interposed between the membranes of the brain of the sperm whale. The other is an oily substance, which has a close relation to vegetable oils. Cétine melts at 120°, and in cooling is reduced to a transparent mass, from which candles are made. It has the common properties of fat bodies. It crystallises either by fusion, or by solution in alcohol or ether, forming brilliant crystals insoluble in water.

Under the influence of alkalies it is transformed into a fat compound, called *ethalic acid*, and a new alcohol called ethal:—

$$\underbrace{C_{64}H_{64}O_4}_{\text{Cétine.}} + KO, HO = \underbrace{KO, C_{32}H_{31}O_3}_{\substack{\text{Ethalate of}\\ \text{potash.}}} + \underbrace{C_{32}H_{33}O, HO}_{\text{Ethal.}}$$

Ethal is solid, fuses at 104°, and when excluded from air volatilises without change. It may be considered as a true alcohol. When treated with sulphuric acid it is transformed into sulphethalic acid, $C_{32}H_{33}O$, $(SO_3)_2$, HO.

Distilled with perchloride of phosphorus it produces a liquid, $C_{32}H_{33}Cl$, which corresponds to the hydrochloric ether of alcohol, C_4H_5Cl.

913. SOAPS are salts formed by the combination of fat acids with metallic oxides. Those which are most common have soda or potash for their base, and margaric, oleic, and palmitic acids as acids.

The only soaps soluble in water are those which have the alkalies for their bases. These are also soluble in alcohol and ether. With the exception of the soaps of copper, of the protoxide of iron and manganese, all the metallic soaps properly so called, are insoluble in these liquids. These latter soaps are also soluble in the fat oils and the essence of turpentine.

The acids in general decompose soaps, combining with their bases, and separating their fat acids, which float at the surface of the aqueous solution, being insoluble in it. The soluble soaps are prepared, either by combining the

fat acids directly with potash or soda, or by heating the oils, fats, or tallows with boiling alkaline solutions. The due management of this process, which is termed *saponification*, requires much time, care, and patience. In the laboratory the process may be imitated by boiling in a porcelain capsule 100 parts of any neutral fat, such as olive oil or tallow, with 20 to 25 parts of caustic potash or soda and 200 to 250 of water. The mixture should be constantly stirred with a glass rod, and the water, as it evaporates, replaced by boiling distilled water. The process may be considered complete when a small quantity of the product is found to dissolve in distilled water without leaving any traces of fatty matter. Complete saponification is also tested by ascertaining whether hydrochloric or sulphuric acid will separate from the soap a fat acid, perfectly soluble in alcohol.

In commerce soaps are distinguished into *soft* and *hard*. Soft soaps have potash, and hard, soda for their base. The former are generally made from oil of hemp, linseed, &c., and the latter from olive oil, tallow, and in general from the better kinds of fat.

Soap is coagulated by a great number of the alkaline and other salts; a property which the manufacturer turns to account, when he thinks that the fatty matters are completely saponified, by separating the soap from the alkaline water by throwing common salt into the vat.

Black soaps and toilet soaps are not thus treated, an excess of alkali being always retained by them; they retain also a variable amount of water.

The soft soaps are more alkaline than the hard, dissolve in water more freely, and, besides the oleate and margarate of potash, they contain excess of potash, chlorides, sulphates, and a part of the glycerine liberated in the saponification.

For it should be remembered that all the oils and fats employed in the soap manufacture are, in reality, true salts; salts, that is, of the various fat acids already mentioned, containing these acids in combination with a base termed oxide of allyle. When these salts are decomposed by more powerful bases, such as potash and soda, the oxide of allyle is displaced, and found as glycerine, the allylic alcohol. This very interesting body, which may be distilled without decomposition, has met with several interesting applications in the arts, and is employed in medicine. It will be found described in § 903.

The fragrance of the scented soaps provided for the toilet proceeds from essential oils, a small quantity of which is mixed with them when liquid, while the disagreeable odour of some of the common soaps arises, either from the resins added in their manufacture, or from the natural smell of the oils employed, as in the case of olive, rape, and palm oils.

914. WAX is obtained from many sources; some varieties are of vegetable, and some of animal origin. Some are found in the leaves, flowers, fruits, and stalks of plants, while others exude from the abdomen of certain hymenopterous insects.

It was long supposed that the bee extracted from flowers the wax with which it forms its comb. The researches of chemists and naturalists have, however, proved this to be an error, the wax being a result of a secretion peculiar to the organism of the insect.

915. BEES'-WAX is the material of which the walls of the cells of the honey-comb are formed. If this be compressed without purification, it will consist of a yellow wax, the point of fusion of which is 143° to 145°. When bleached white by exposure to air

it fuses at 147° to 149°. This bleached wax, before the discovery of the methods of preparing stearine, was largely used in the manufacture of candles.

PARAFFINES, hydrocarbons obtained from peat and other similar substances, are now largely employed for illuminating purposes, and for lubricating machinery.

CHAPTER XXIX.

COLOURING MATTERS.

916. COLOURING MATTERS are universally diffused in all parts of the organic world, in the roots, wood, bark, stalks, leaves, flowers, fruits, and seeds of vegetables; in the bodies of insects; and in the fluids of the animal body. They are rarely found already isolated, and it is often difficult to disengage them from their combinations. Sometimes they do not pre-exist in organic compounds, but are developed by fermentation, by oxidation, or under the influence of alkaline agents.

The most frequent colouring principles are yellow, red, and green. The yellows and reds are in general easily isolated; the greens are more difficult. The green principle of foliage, which plays so important a part in the theatre of nature, and is called *chlorophyll*, has never yet been obtained in a state of perfect purity.

The following are examples of vegetable colouring principles:—

Yellow. Curcumine or turmeric, gamboge, annatto, carotine, rhubarberine, luteoline, quercetrine, morine, safflower, polychroite, monidine.

Red. Dragon's blood, santaline, anchusine, carthamine, madder, logwood, Brazil wood, camwood.

Blue. Chiefly from flowers and fruits, all turned green by alkalies, and red by acids.

Green. Chlorophyll, the essential colouring principle of leaves.

917. Besides the peculiar properties of each form of colouring matter, these principles have some general characters which it will be useful to notice.

They have often a sweetish and somewhat acrid taste, and are inodorous. Some (EX.: indigotine and alizarine) are easily crystallised. They are often volatile, but should be distilled at a temperature below 300°, at which they are decomposed. All absorb oxygen under the influence of light, undergoing a slow incipient combustion, and are thus bleached. They are said to be more *fast* as they are less susceptible of this change.

They are often soluble in water. Some are only soluble in alcohol, ether, or the essential oils. The presence of acids favours the solution of some (hematosine, indigotine, alizarine, purpurine), of alkalies others (carthamine, santaline).

918. The tints produced by colouring matters are modified and varied in a definite manner by chemical agents. This property is rendered useful in dyeing and calico-printing, and also in chemical analysis. Thus, the processes of alkalimetry and the analysis of borax are based upon the different tints imparted to litmus by weak acids, such as carbonic and boracic, and by strong acids, such as sulphuric.

919. The bases, when concentrated, decompose all the colouring principles, but when diluted only modify their tints. This circumstance is also turned to account by the dyer and calico-printer. In some cases the colours are developed under the influence of the bases and of oxygen. An example of this is presented in the case of tannin, which, according to Chevreul, forms colouring matter of a reddish-brown colour when submitted to the influence of oxygen and an alkali.

920. In many cases varieties of tint are produced by the combination of colouring matters with the metallic oxides, the former in such cases playing the part of acids. Thus, *lakes* are nothing more than compounds of colouring matters with alumina. The colouring principle in yellow lakes is a decoction of Persian or French berries (*Rhamnus infectorius*), quercetron, or annatto; that of red lakes carmine.

921. Several salts act by their oxide or base on colouring matters, entering into combination with them, and fixing them upon the stuff or cloth. It is upon this principle that the use of *mordants* is based.

Pulverised charcoal and animal black absorb, but do not destroy, colouring matters. The colouring matter absorbed may be recovered in many cases under the influence of slightly alkaline liquor.

922. No known colouring matter can resist chlorine. All undergo a real combustion under the influence of this powerful agent, dismissing hydrogen, which is transformed into hydrochloric acid, and attracting chlorine. In such cases it appears that, under the influence of an aqueous solution of chlorine, water is decomposed, its hydrogen combining with chlorine to form hydrochloric acid, and its oxygen reacting upon and decomposing the colouring matter. Since the results of the experiments of Berthollet have been known, tissues intended to be dyed or printed are in most cases previously bleached with chlorine.

923. Sulphurous acid exercises a reaction on colouring matters, which is of great importance in the arts, usually destroying the colouring principle without affecting the tissue. It is especially applied to bleach silk and wool. It acts, sometimes by dismissing the oxygen, and sometimes by combining with the colouring matter to form a colourless compound. It is also supposed that it decomposes the water, seizing upon the oxygen, while the hydrogen combining with the colouring matter forms a colourless compound. It is well known that fruit stains may be removed from linen by sulphurous acid; but in this case it is necessary to wash the linen carefully to dissolve the sulphuric acid produced by the combination of the oxygen of the decomposed water with the sulphurous acid, which, if allowed to remain, would destroy the fibres of the tissue.

924. Certain bodies, which have a strong affinity for oxygen, bleach colouring matters by an action so feeble that their colours are restored by mere exposure to the air. Among these are hydrogen, sulphurous acid, hydrosulphate of ammonia, the alkaline sulphurets, and the protoxide of iron. Their action is explained by some chemists by the supposition that they decompose the water, absorbing the oxygen and liberating the hydrogen, which combines with the colouring matter to form a colourless compound. Others, on the contrary, think that the colouring matters are deprived of their oxygen, and thereby of their colour, under the influence of these bodies.

925. Tissues absorb colouring matters; a sort of mechanical combination takes

place between the colouring principle and the tissue, which, however, is not a combination in definite proportions. It is on this principle that the art of dyeing is founded.

All tissues have not equal affinities for colouring matters. Those which are of animal origin, such as silk and wool, absorb the colouring principles most readily. Cotton, hemp, and flax have this property in a much less degree.

The composition of colouring matters is very various. Some consist of carbon, hydrogen, and oxygen; others include nitrogen. The hydrogen and oxygen are found in some in the proportion to constitute water.

926. INDIGO, $C_{16}H_5NO_2$, incomparably the most important of the colouring principles, is extracted from a class of plants which have received the common name *indigofera*, and which are objects of cultivation in China, Japan, India, Egypt, and America.

The indigo of commerce is more or less impure. When rendered by certain processes chemically pure it is called *indigotine*. 18 parts by weight of indigo of commerce contain 6 of pure indigo or indigotine. Various processes of purification are practised, one of the most simple of which consists in the distillation of the indigo of commerce.

Indigotine is unalterable in air, odourless and tasteless, insoluble in water and ether, soluble in a small proportion in alcohol, and volatilised without decomposition when thrown upon a heated metallic surface.

By the reaction of sulphuric acid upon it three double acids are formed, the most important of which is *sulphindigotic acid*, which is used in dyeing. This is almost always accompanied by another acid, called *sulphopurpuric acid*.

927. Deoxidating bodies exercise an action on indigo, which is rendered useful in the arts. They decompose the water, absorbing its oxygen and liberating its hydrogen, which combining with the blue indigo converts it into white indigo, which is soluble in water, and may, under the influence of air, be reconverted into blue indigo.

928. WHITE INDIGO is solid, crystalline, silky, heavier than water, inodorous, tasteless, without action on litmus, insoluble in water, and soluble in alcohol and ether. Under the influence of oxygen it is rapidly converted into blue indigo.

$$\overbrace{C_{16}H_6NO_2}^{\text{White indigo.}} + O = \overbrace{C_{16}H_5NO_2}^{\text{Blue indigo.}} + HO.$$

929. LITMUS, so useful as an acid and alkali test in the laboratory, is a colouring matter obtained by submitting certain lichens (variolaria, lecanora, &c.) to putrefaction in the presence of ammonia and air. It does not pre-exist in the plant, but is produced by the reaction of the ammonia upon a neutral non-nitrogenous substance called *orcine*, which itself proceeds from the decomposition of several colourless and crystallisable principles

contained in the lichens, such decomposition being produced under the influence of alkalies.

930. LOGWOOD gives an aqueous extract, which treated with alcohol or ether gives a slightly coloured matter called *hematoxyline*, which under the influence of oxygen and ammonia is transformed into the colouring matter *hemateine*.

931. MADDER (*Rubia tinctorum*), the essential principle of which is alizarine, $C_{30}H_8O_8$*, is one of the most important of the tinctorial products. According to Schunck, the madder root contains 7 different substances; viz., 2 colouring matters, *alizarine* and *rubiacine*, a bitter principle *rubiane*, two resins, pectic acid, and finally a brown substance, which probably results from oxidation.

CHAPTER XXX.

ANIMAL COMPOUNDS.

932. ANIMAL chemistry consists of the exposition of the immediate constituents of the animal organism, of the chemical and physiological properties of the principal liquids and tissues which form it, and of the chemical phenomena developed in it as well under the influence of life as after death.

933. UREA, $C_2N_2H_4O_2$, is a crystalline substance which exists in urine, and which may be artificially produced by the metamorphosis of cyanate of ammonia—

$$\underbrace{NH_3,HO,C_2NO}_{\text{Cyanate of Ammonia.}} = \underbrace{C_2N_2H_4O_2}_{\text{Urea.}}$$

Urea constitutes nearly half the solid matter which urine holds in solution. A man discharges a mean quantity of from 1 oz. to 1½ oz. of urea per day, and as this does not contain less than one-third of its weight of nitrogen, it follows that the chief part of the nitrogen contained in food passes off in this way.

Urea crystallises in long four-sided prisms. It is when pure colourless, inodorous, and of a cooling taste like that of nitre. It is very soluble in water, less so in alcohol, and scarcely so in ether. It has the properties of a base, forming definite salts with acids, which are anhydrous for the hydracids, and which for the oxacids contain 1 equivalent of water. It differs nevertheless from other organic bases, inasmuch as it does not restore the colour to litmus reddened by an acid, is generally without action on the colour tests, and by a remarkable exception, is incapable of combining with certain acids, such as lactic, hippuric, carbonic, hydrosulphuric, and others.

It melts at 248°, and is decomposed at a somewhat higher

* $C_{28}H_8O_6$, Regnault.

temperature, being resolved into ammonia which is disengaged, and a residuum of cyanuric acid.

934. ALBUMINOUS COMPOUNDS found in the animal organism are chiefly albumen properly so called, fibrine, caseine, &c. All such bodies have been supposed to result from the combination of sulphur, phosphorus, and certain salts with a nitrogenous compound called *proteine*.

935. PROTEINE, $C_{40}H_{31}N_5O_{12}$, obtained by treating albumen or caseine successively by water, alcohol, and ether, is white, inodorous, and insipid. It attracts humidity from the air, and is decomposed by heat, giving all the products which characterise the distillation of nitrogenous bodies. It is insoluble in water, alcohol, and ether, and forms definite combinations with both alkalies and acids. When boiled with potash it is decomposed, disengaging ammonia. The ferro- and ferrid-cyanides of potash precipitate it from its solutions in the alkalies. It is dissolved by long continued ebullition.

936. FIBRINE is a substance held in suspension in blood, and imparts to that fluid its coagulability. It constitutes the chief part of the substance of the muscles.

When blood is taken from the vessels it separates into two distinct parts, a sort of jelly called *clot*, and a liquid called *serum*. The fibrine is exclusively contained in the clot. It is by it that the red globules which impart its characteristic colour to the blood are held, as it were, in a sort of network. These globules may be separated from the fibrine by cutting the clot in thin slices, placing it in a canvas strainer, and passing water through it. The globules will be carried off with the water, and the fibrine will remain in the strainer as white elastic filaments.

Fibrine, when pure, is white and completely insoluble in water, alcohol, and ether. When burned it leaves 2 or 3 per cent. of ashes, consisting chiefly of phosphates of magnesia and lime.

937. ALBUMEN is a compound common to the animal and vegetable worlds, and most universally diffused throughout nature. It is considered by Mülder as proteine combined with some traces of sulphur and phosphorus. It is found in a state of solution in some liquids of the animal organism, such as the blood and the white of egg.

Submitted to a temperature of 149° it becomes opaline, and at 167° it is completely coagulated. Chevreul has shown that the coagulation is due to a true isomeric modification, and that it takes place without any loss of water. In the act of coagulation it collects all the bodies suspended in the liquid in a sort of network, and in virtue of this property is employed for the clarification of liquors.

938. According to Dumas and Cahours the centesimal composition of albumen is:—

Carbon	53·59
Hydrogen	7·27
Nitrogen	15·72
Oxygen	23·42
	100·00

939. CASEINE is an albuminous substance found in milk. It is white, scarcely soluble in water, and quite insoluble in

alcohol. It is soluble in the alkalies. The acids precipitate it and have a tendency to combine with it. It slightly reddens litmus paper.

940. GELATINE, $C_{13}H_{10}N_2O_5$, is obtained from the skin, bones, cartilages, and other tissues by boiling them in water. That which is obtained from cartilage having somewhat different properties is called *chondrine*, $C_{32}H_{26}N_4O_{14}$. This latter is precipitated from its solutions by almost all the acids, but the precipitate is soluble in an excess of the reagent. Carbonic acid also precipitates it.

According to Mülder the centesimal composition of gelatine is :—

Carbon	50·07
Hydrogen	6·25
Nitrogen	19·32
Oxygen	24·27

The difference between the total (99·91) and 100·00 is owing to traces of other substances not mentioned, and to unavoidable loss in the analysis.

Gelatine, which is identical with pure glue, is colourless and transparent. It possesses cohesiveness in a remarkable degree. It is inodorous, insipid, and neutral to the colour tests. When heated it is first fused and then decomposed, diffusing a disagreeable odour of burnt horn. It is softened, but not dissolved by cold water. It is in this case hydrated, absorbing about six times its weight of water.

It is dissolved by boiling water, and in cooling takes the consistency of jelly. A solution which contains no more than 1 per cent. of gelatine will form a jelly in cooling. Such a jelly acidifies under the influence of heat.

941. BLOOD. The characters of this important fluid mechanical and physiological are fully explained in the special works on anatomy and physiology.* Nevertheless, its properties will require some brief notice here.

Human blood, and that of mammifers generally and birds, is an alkaline liquid, thick and viscous, somewhat heavier than water. It has a peculiar heavy odour and disagreeable saltish taste; qualities which vary more or less in different animals, and in some are characteristic. Its alkaline quality is due to the presence of soda, and is essential to its vital functions. Its colour varies in different classes, being dark red in reptiles, bluish in fishes. Of invertebrates the leech alone has red blood. In certain mollusca (Biphora) it is colourless, in others (Gasteropods) it is slightly varied in colour, and of a milkish blue. In insects that of the dorsal vessel is transparent, and in several orthoptera of a greenish tint. In the silkworm it is yellow, and in the willow caterpillar, orange. In most of the coleoptera it is dark brown. In the echinodermata it is yellow or orange.

At 60° F. human blood in the adult has SG = 1·050 to 1·058. Its temperature in the heart of the mammals varies from 100° to 104°; while in birds it is from 7° to 9° higher.

The serum, the yellowish liquid which constitutes about ⅘ of the blood has SG = 1·027 to 1·029. The red and more solid part is termed *the clot*.

* See also Animal Physics, Chap. VI. and Physiology for Schools, Chap. VI.

942. According to Dumas the following is the mean centesimal composition of the venous blood of a man in health :—

Serum	870
Clot	130
	1000

943. Hematosine, the colouring principle of the blood, is a brownish solid without taste or odour. Its solution in ammoniacal alcohol evaporated in a water-bath gives a mass of a blackish red colour, with a metallic appearance. It is insoluble at all temperatures in water, alcohol, ether, and the oils, whether fixed or volatile, except the oil of turpentine and olive oil, in both of which when hot it is soluble.

944. BILE is a liquid secreted in the liver, received in the gall-bladder and poured from it into the small intestine immediately below the point where it issues from the stomach. Its physiological uses are explained elsewhere.* It is yellowish and sometimes green, soluble in all proportions in water, of a taste bitter at first, and then sweetish, often alkaline, but sometimes neutral. Its composition is very complex. It is aqueous, containing several salts, some albuminous matters, and chiefly a sort of soap with a base of soda.

The biliary concretions sometimes found in the gall-bladder generally consist of a fat crystalline substance called *cholesterine*.

945. BONES consist of an organic constituent convertible into gelatine by continued boiling, and an inorganic part. The former is usually 33, and the latter 67 per cent. of the entire bone. The inorganic part consists of 54 parts of tribasic phosphate of lime, $(CaO)_3,PO_5$, 11 of carbonate of lime, 1 of phosphate of magnesia with traces of fluoride of calcium and alkaline salts. Treated with acids they lose their inorganic constituent, and a cartilaginous residuum is obtained easily transformed into gelatine by boiling.

946. MILK secreted in the mammary glands is white, opaque, and alkaline. Its SG = 1·02 to 1·04. It, in woman, contains 2 to 2·75 per cent. of butter, 4 to 5 of sugar of milk, 3 to 4 of cheesy matter, some salts, and about 90 of water.†

* Animal Physics (692); Physiology for Schools, Chap IX.
† Animal Physics (1113).

THE END.

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